Iodine in seaweed - occurrence, speciation, bioavailability and risk assessment

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EWCPS2017

EUROPEAN WINTER CONFERENCE ON PLASMA SPECTROCHEMISTRY

SANKT ANTON, ARLBERG - AUSTRIA
19. – 24 FEB. 2017

ORGANIZATION

University of Natural Resources and Life Sciences Vienna

in collaboration with the

Helmholtz-Centre for Materials and Coastal Research

ORGANIZING TEAM

Thomas Prohaska (Chair)
Johanna Irrgeher (Co-Chair)
Stephan Hann
Daniel Pröfrock
Andreas Zitek

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EWCPS 2017

“There is in truth only atoms and emptyness”

– Democritus

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1.1 PREFACE

„After 1989 in Reutte and 2009 in Graz, the European Winter Conference on Plasma Spectrochemistry is held again in Austria. The University of Natural Resources and Life Sciences Vienna and the Helmholtz Centre, Geesthacht, shared efforts to setup a splendid conference at a unique venue in the heart of Europe, in the middle of the alps. Plasma spectrochemistry has become a mature technique and the community is growing but still it offers fascinating developments and a familiar atmosphere. I am looking forward to sharing novel insights, creative inpputs or just the pleasure to spend time together.“ *Thomas Prohaska (Chair of EWCPS2017)*

„EWCPS has evolved as integral part of the scientific calendar in the area of plasma spectrochemistry meeting the interests and needs of researchers working in very different contexts, spanning from fundamental plasma physics to various fields of application. As we know that there are many conferences to choose from these days and budgets are always tight, it is very satisfying to see such a great number of participants and scientific contributions this year. With this I wish all of us many new and exciting ideas and inspiring discussions as well as a beautiful week in the Austrian winter in St. Anton.“ *Johanna Irrgeher (Co-chair of EWCPS2017)*

„Having worked in the field of ICP-MS for more than 20 years, it is my great pleasure to be part of the organizing committee of this wonderful conference series. I have enjoyed (and am still enjoying) working in the field of elemental analysis although my group and I have extended the scope of research to molecular mass spectrometry during recent years. St. Anton is part of Arlberg, which is my favourite skiing region – I learned to ski in these mountains. Hence, I am very confident that the scientific program and enjoying the outdoors will be a perfect combination to make this conference both successful and unforgettable!“ *Stephan Hann*

„If I take a closer look at the technique that significantly rules the daily life of most of us namely ICP-MS as well as the related ongoing developments, I always ask my self ‚What will be next?‘ Over the decades ICP-MS has clearly matured to an irreplaceable key tool for element, isotope and speciation analysis as well as imaging applications. However also during the last two years since the 2015 EWCPS held in Münster again much progress has been made, which will become visible during the lectures and poster sessions as well as at the booths of the different instrument manufacturers at the EWCPS2017 in Sankt Anton.“ *Daniel Pröfrock*

„Plasma based mass spectrometry has become a major technique in analytical chemistry in a variety of different scientific disciplines. Analytical developments and transdisciplinary research conducted by domain experts in strong collaboration with analytical chemists have led to an everongoing expansion of both the analytical methods and capabilities and the domain specific methods, results and future research possibilities. The focus of the conference has ever been to share fundamental developments in instrumentaion and analytical procedures together with inspiring new applications of different types of plasma-based spectrochemistry in scienctific fields. Welcome to the EWCPS 2017 in Sankt Anton, Austria, the heart of Europe!“ *Andreas Zitek*

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AWARDS

In the course of the EWCPS2017, several awards and grants were given to outstanding both emerging and established scientists in the field of plasma spectrochemistry:

“EUROPEAN AWARD FOR PLASMA SPECTROCHEMISTRY” and the new “EUROPEAN RISING STAR AWARD FOR PLASMA SPECTROCHEMISTRY” were sponsored by Agilent Technologies Inc. .

„NEW EMERGING LEADER IN ATOMIC SPECTROSCOPY AWARD“ was sponsored by Spectroscopy Magazine.

„EWCPS YOUNG SCIENTISTS GRANT“ was established by the EWCPS2017 organizers and sponsored by EWCPS2017.

“EUROPEAN AWARD FOR PLASMA SPECTROCHEMISTRY”

The “European Award for Plasma Spectrochemistry”, which promotes analytical plasma spectrochemical developments and applications in Europe, is awarded for a single outstanding piece of work or for continued important contributions in the field.

The Agilent PLASMA AWARD is awarded to Joanna Szpunar, National Research Council of France (CNRS), for her innovative contributions in the field of metallomics and bio-organic speciation, her significant scientific contributions and her support of the plasma spectrochemistry and inorganic mass spectrometry community.

JOANNA SZPUNAR graduated from the Warsaw University of Tec hnology in 1986 and obtained her Ph.D (1992) and D.Sc. (habilitation) (2000) from at the University of Warsaw. Since 1997 she works at the National Research Council of France (CNRS). In 2007 she obtained the title of professor of chemistry (Poland). Her research interests concern bioinorganic speciation analysis and hyphenated techniques for metallomics. She was the chairperson of the Winter Conference on Plasma Spectrochemistry in 2013.

„It is with great interest and pleasure that I am looking forward to the European Winter Conference on Plasma Spectrochemistry 2017 in Sankt Anton. For more than 20 years I have been one of the “regulars” of this series of conferences. I appreciate the winter conferences not only as a recognized forum of exchange on diverse topics concerning analytical plasma spectrochemistry, but also as an opportunity to meet old friends and make some new ones. This double feature of continuity and change is always reflected by the same (winter) season when it is held, and the changing venues including the 2017 setting which is expected to be full of snowy blessings. I am sure that the high quality of the formal presentations and informal discussions, the high level of new instrumental developments shown during the vendors’ events, and the attractiveness of the social programme will make this conference professionally fruitful and entertaining for all the participants.

The 2017 EWCPS meeting is definitely a very special one for me personally as the awardee of the European Award for Plasma Spectrochemistry. This is a great honor and I am truly grateful to the Award Committee for the recognition of my work. I profit here to sincerely thank my colleagues, post-docs and students and the whole team working at the Laboratory of Analytical Bio-Inorganic and Environmental Chemistry in Pau for their inspiration and everyday support. The honor is even greater when I think about my predecessors including the only awardee, so far, coming from a French laboratory and being one of plasma spectrochemistry classics - Jean-Michel Mermet. I hope to be able to continue my work and keep contributing to the coming EWCPS meetings with new exciting data and look forward to all the scientific challenges that are waiting for me in the future.“ *Joanna Szpunar*

“EUROPEAN RISING STAR AWARD FOR PLASMA SPECTROCHEMISTRY”

The new “European Rising Star Award for Plasma Spectrochemistry” should honor and promote outstanding contributions of upcoming younger scientist at the beginning of their career within the field of plasma spectrochemistry.

The Agilent RISING STAR PLASMA AWARD will be awarded to Johanna Irrgeher, HZG Geesthacht, a promising young scientist, who has contributed with highly important work in an area of increasing significance, namely isotope ratio MS. She is awarded for her significant fundamental research and novel exciting applications of isotope ratio MS and her outstanding scientific record.

JOHANNA IRRGEHER is currently postdoctoral researcher in the field of analytical chemistry at the Helmholtz Centre for Materials and Coastal Research Geesthacht in Germany with her research focus set on analytical method development for elemental and isotopic analysis in the field of analytical ecogeochemistry dealing with aquatic and terrestrial ecosystems.

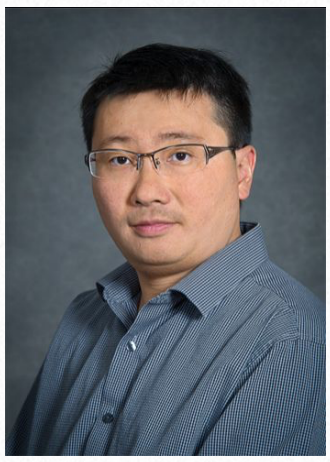
„Being awarded the newly initiated ‚European Rising Star in Plasma Spectrochemistry Award’ is certainly a great honor. At the outset, I would like to express my gratitude to the nominators for nomination and to the award committee for selection, but above all to Agilent Technologies, who have created this award only recently. Besides acknowledging renowned scientists in the field of plasma spectrochemistry with the well-known Plasma Award, this prize shows the respect towards young scientists, currently developing in the field and definitely encourages continuing in research.It is a great honor for me personally to be the first scientist given this award. As a young Postdoc in analytical chemistry, currently working in the field of environmental research at the Helmholtz-Centre Geesthacht (Germany), the award also emphasizes the relevance of the work I am doing.

I am very thankful to a great number of people, who accompanied and supported my way in this research field. I would like to point out though that the ICP-MS community always conveyed a sense of warm acceptance and openness, also to young people even at the early start of their careers, independent of their status in research or academia. This cozy ambience surely makes working in the field very enjoyable. I have experienced this feeling since my first attendance to the European Winter Conference 2009 in Graz as a master student and since then, I have always enjoyed the meeting very much. As awardee but also organizer of this year’s EWCPS, I am very much looking forward to an interesting, stunning and also entertaining meeting in the middle of the Austrian Alps in a very beautiful area of my home country.“ *Johanna Irrgeher*

“EMERGING LEADER IN ATOMIC SPECTROSCOPY AWARD”

The „Emerging Leader in Atomic Spectroscopy Award“ recognizes the achievements and aspirations of a talented young atomic spectroscopist who has made strides early in his or her career toward the advancement of atomic spectroscopy techniques and applications.

The Emerging Leader in Spectroscopy Award 2017 goes to George CHAN from Lawrence Berkeley National Laboratory in Berkeley, California.



GEORGE CHAN is currently a Project Chemist at the Lawrence Berkeley National Laboratory. Prior to joining LBNL in 2012, he was an Assistant Scientist on the research faculty in the Department of Chemistry at Indiana University. He received a Ph.D. degree in Analytical Chemistry under the mentorship of Prof. Gary Hieftje at Indiana University in 2007.

„I am George Chan and am profoundly honored to receive the inaugural Emerging Leader in Atomic Spectroscopy Award, and to have this opportunity to present my research at the 2017 European Winter Conference on Plasma Spectrochemistry. This annual award, presented by Spectroscopy magazine and selected by an independent committee, is a very valuable recognition of my achievements in analytical atomic spectrometry. I appreciate Spectroscopy for creating this award as a way to recognize and encourage the next generation of atomic spectroscopists, and understanding how valuable recognition of this type is to a young researcher.

I am currently a project scientist at the Lawrence Berkeley National Laboratory (LBNL), California, USA. Prior to joining LBNL in 2012, I was an Assistant Scientist on the research faculty in the Department of Chemistry at Indiana University. I received a Ph.D. degree in Analytical Chemistry under the mentorship of Prof. Gary Hieftje at Indiana University in 2007. My research interest involves both fundamental and practical aspects of plasma spectrochemistry. Some examples include: understanding the matrix effects and excitation processes in the inductively coupled plasma (ICP), development of automatable plasma-diagnostic tools to flag the presence of interferences in ICP-OES measurements and methods to alleviate them, characterization of fundamental mechanisms in plasma sources used in ambient ionization mass spectrometry, and optical isotopic analysis with laser induced breakdown spectroscopy (LIBS) and laser ablation molecular isotopic spectrometry (LAMIS). I have attended the European Winter Conference on Plasma Spectrochemistry twice before (Budapest 2005, Taormina 2007), and have been impressed by the conference organization, presentations and the interaction opportunities with other scientists. I look forward to the 2017 EWCPS at Sankt Anton am Arlberg. I would like to thank Spectroscopy for presenting and the independent scientific committee for selecting me for this prestigious award, and the organizing committee of the 2017 EWCPS for inviting me to the conference.“ *George Chan*

“EWCPS YOUNG SCIENTISTS GRANT”

A number of grants for PhD students with oral contributions to the conference with high scientific impact are provided. Applications were be judged by the scientific committee. More than 30 grant applications had to be evaluated. Ten PhD students were finally awarded with the EWCPS2017 Young Scientists Grant.

The grants are sponsored by EWCPS2017, Berghof and Ramon Barnes, chair of the WCPS, supports their participation at the WCPS 2018.

DIEGO BOUZAS RAMOS

Affiliation: Dept. of Physical and Analytical Chemistry, University of Oviedo, Spain

Topic: Determination of the stoichiometry CdSe/ZnS quantum dot to antibody in bioconjugates by asymmetric flow field-flow fractionation coupled on-line to elemental mass spectrometry (ICP-QQQ) (*award sponsored by Berghof*)

„I would like to take this opportunity to express my sincere gratitude to the scientific and organizing committees for selecting me as a recipient of the EWCPS 2017 Young Scientists Grant. I am so humbled and honored to have been chosen for this student grant award knowing that there were many qualified applicants. Once again, thank you so much for allowing me to live this enriching and life-enhancing experience.“ *Diego Bouzas Ramos*

MARÍA CRUZ-ALONSO

Affiliation: Analytical Spectrometry Research Group; Dept. of Physical and Analytical Chemistry, University of Oviedo, Spain

Topic: Quantitative imaging of potential protein biomarkers in oral cancer tissues with LA-ICP-MS using bioconjugated gold nanoclusters

„María is a Ph.D. student at Analytical Spectrometry Research Group (University of Oviedo, Spain) under the supervision of Ph.D. Rosario Pereiro and Ph.D. Beatriz Fernández. The current topic of her Ph.D. is “Development of an analytical methodology based on metal nanoclusters as labels in immunoassays coupled to bioimaging, for the determination and quantification of potential protein biomarkers”. Maria wants to thanks to the Scientific Committee of EWCPS2017 for the Young Scientific Grant.“ *Maria Cruz Alonso*

HANNAH HOLTKAMP

Affiliation: Bioionorganic and Medicinal Chemistry Hartinger Lab, The University of Auckland, NZ

Topic: Towards routine capillary electrophoresis hyphenation to ICP-MS

„I would like to extend my utmost gratitude to the organisers of the EWCPS for providing the Young Scientists Grant and selecting me as one of the recipients. Traveling from Auckland, New Zealand, I feel highly privileged to have the opportunity to attend this prestigious conference to share and discuss my research in such an a-we-inspiring location on the other side of the planet.“ *Hannah Holtkamp*

BALÁZS KLENCSÁR

Affiliation: University of Ghent, Department of Analytical Chemistry, Ghent, Belgium

Topic: Determination of the total content of drug-related chlorine and chlorine speciation in human blood plasma using high performance liquid chromatography – tandem ICP- mass spectrometry (HPLC-ICP-MS/MS)

„I hereby would like to thank the Scientific Committee of EWCPS2017 for providing me with the Young Scientists Grant which makes my participation in one of the most prestigious conference of the field possible. I would like to also acknowledge my promotor, Prof. Dr. Frank Vanhaecke for the continuous support during my work.“ *Balázs Klencsar*

THIAGO LINHARES MARQUES

Affiliation: Group for Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, Brazil

Topic: Application of high pressure microwave-assisted digestion flow system for juice and milk sample preparation

"Scientists are dreamers who enjoy making unexpected things become real." - *Thiago Linhares Marques*

ANIKA RETZMANN

Affiliation: University of Natural Resources and Life Sciences, Vienna, Department of Chemistry, Division of Analytical Chemistry, VIRIS Laboratory, Austria

Topic: Spectral insights: Multi-dimensional approach to evaluate the diagenetic status of skeletal remains with respect to strontium isotope ratio measurements

„(Sr) Isotopic Analysis, MC ICP-MS, MEA, ICP-MS, LA, Diagenesis, Imaging, Solubility Profiling, Migration/Mobility, and HSI, these are the key words of my PhD. So there will be quite a lot to learn for me at the EWCPS2017 and I am glad, that I will get the chance to present and discuss my ongoning PhD research to/with such a sophisticated, international audience.“ *Anika Retzmann*

CARLOS SÁNCHEZ RODRÍGUEZ

Affiliation: Department of Analytical Chemistry, Nutrition and Food Sciences. University of Alicante, Alicante, Spain

Topic: Fundamental studies on the ions distribution in ICP-MS for ethanol-water matrices and its application to the determination of metals in bioenthanol

„I would like to express my great appreciation to the EWCPS2017 organizing and scientific committees for promote and facilitate the participation of young researchers in this amazing conference. I am sure that we will exploit this opportunity to network with other researchers and professionals, exchange experiences and disseminate our main results. Thank you for making it possible!“ *Carlos Sanchez Rodriguez*

JUSTYNA WOJCIESZEK

Affiliation: Chair of Analytical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland

Topic: Single particle ICP-MS characterization of engineered nanoparticles uptake and bioaccumulation by edible plants

„I would like to sincerely thank the Scientific Committee of European Winter Conference on Plasma Spectrochemistry for appreciating my work and awarding me with the EWCPS2017 Young Scientific Grant. My contribution is the result of my scientific stay at Laboratoire de Chimie Bio-Inorganique Analytique et Environnment in Pau, France. I would like to express my gratitude to the whole staff for the support provided.“ *Justyna Wojcieszek*

ZAKON YEVGENI

Affiliation: Department of Chemistry, The Hebrew University, Jerusalem, Israel

Topic: Development of $\delta^{37}Cl$ isotope analysis by Ion Chromatography/MC-ICPMS and its application for studying biodegradation of perchlorate

„I would like to thank the organizing committee for the award and the opportunity to present my work at EWCPS 2017.“ *Zakon Yevgeni*

LINGNA ZHENG

Affiliation: Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China

Topic: Quantitative analysis of Gd@C82(OH)22 and cisplatin uptake in single cells by inductively coupled plasma mass spectrometry

„It is my great honor to be one of the student grant winners. Taking part in the excellent EWCPS2017 will definitely be important milestone in my life.“ *Lingna Zheng*

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PROGRAMME

“If we knew what it was we were doing, it would not be called research, would it?.”

– Albert Einstein

SUNDAY, 19 FEB

09:00 - 12:00	Short courses and technical meetings
13:00 - 16:00	Short courses and technical meetings
16:00 - 18:00	Ice Breaker EWCPS2017 Winter Market
18:00 - 18:20	EWCPS2017 Grand Opening
18:20 - 19:20	Opening lecture - Sam Houk
19:20 - 19:30	Spectroscopy Award
19:30 - 19:40	Agilent Plasma Rising Star Award
19:40 - 19:50	Agilent Plasma Award
19:50 - 21:40	OPENING Vendors exhibition Wine&Cheese and award winner reception

MONDAY, 20 FEB

SESSION 1 - FUNDAMENTALS

08:30 - 09:00	Plenary lecture - Jacob Shelley
09:00 - 09:20	Invited lecture - Annemie Bogaerts
09:20 - 10:20	Lecture session
10:20 - 11:00	Coffee break – Vendors exhibition
11:00 - 12:20	Lecture session
12:20 - 13:40	Lunch break – Vendors exhibition
13:40 - 14:00	Invited lecture - George Chan
14:00 - 14:20	Invited lecture - Steven Ray
14:20 - 15:30	Lecture session
15:30 - 16:10	Coffee break – Vendors exhibition

SESSION 2 - METROLOGY

16:10 - 16:40	Plenary lecture - Lu Yang
16:40 - 17:00	Invited lecture - Heidi Goenaga-Infante
17:00 - 17:20	Invited lecture - Michael E. Wieser
17:20 - 17:40	Invited lecture - Thomas Walczyk
17:40 - 18:00	Invited lecture - Wolfhard Wegscheider
18:00 - 19:20	Lecture session
19:30 - 21:10	LIBS Workshop hosted by Applied Spectra - Vendors exhibition

TUESDAY, 21 FEB

SESSION 3 - SPECIATION

08:30 - 09:00	Plenary lecture - Joanna Szpunar
09:00 - 09:20	Invited lecture - Walter Gössler
09:20 - 10:10	Lecture session
10:10 - 10:40	Coffee break - Vendors exhibition
10:50 - 12:20	Vendors session
12:20 - 14:00	Lunch break - Vendors exhibition Lunch seminar hosted by Agilent (Arlbergsaal)
14:00 - 15:40	Poster exhibition
15:40 - 16:40	Lecture session
16:40 - 17:20	Coffee break - Vendor exhibition
17:20 - 18:30	Lecture session
20:30 - 23:00	Après Plasma Party - @POSTKELLER&PICCADILLY St.ANTON

WEDNESDAY, 22 FEB

SESSION 4 - ISOTOPE RATIO ANALYSIS

08:30 - 09:00	Wake-up coffee - Vendors exhibition
09:00 - 09:30	Plenary lecture - Frank Vanhaecke
09:30 - 09:50	Invited lecture - Mark Rehkämper
09:50 - 10:10	Lecture session
10:10 - 10:50	Coffee break - Vendors exhibition
10:50 - 11:10	Invited lecture - Johanna Irrgeher
11:10 - 12:00	Lecture session
12:00 - 13:40	Lunch break - Vendors exhibition Lunch seminar hosted by Thermo (Arlbergsaal)
13:40 - 14:00	Invited lecture - Sylvain Berail
14:00 - 14:40	Lecture session
14:40 - 15:20	Coffee break - Vendors exhibition

SESSION 5 - METALLOMICS

15:20 - 15:50	Plenary lecture - Gunda Köllensperger
15:50 - 16:10	Invited lecture - Maria Montes-Bayón
16:10 - 17:50	Lecture session
18:00 - 20:00	Young Scientists career event - Vendors exhibition / Evening social mixer at ESI/Meinhard booth

THURSDAY, 23 FEB

SESSION 6 - NANOMATERIAL ANALYSIS (Arlbergsaal)

08:30 - 09:00	Plenary lecture - Björn Meermann
09:00 - 09:20	Invited lecture - Carsten Engelhard
09:20 - 10:10	Lecture session
10:10 - 10:50	Coffee break - Vendors exhibition
10:50 - 11:10	Invited lecture - Frank Von der Kammer
11:10 - 11:30	Invited lecture - Bernd Bodenmiller
11:30 - 12:10	Lecture session
12:10 - 13:50	Lunch break Lunch seminar hosted by Teledyne Cetac (Hotel Post)
13:50 - 15:40	Lecture session

SESSION 7 – LASER-ASSISTED ANALYSIS / GLOW DISCHARGE

08:30 - 09:00	Plenary lecture - Richard Russo
09:00 - 09:20	Invited lecture - Alex Gundlach-Graham
09:20 - 10:10	Lecture session
10:10 - 10:50	Coffee break - Vendors exhibition
10:50 - 11:10	Invited lecture - Jorge Pisonero
11:10 - 11:30	Invited lecture - Bodo Hattendorf
11:30 - 12:10	Lecture session
12:10 - 13:50	Lunch break - Vendors exhibition Lunch seminar hosted by Teledyne Cetac (Hotel Post)

SESSION 8 - BIOIMAGING

13:50 - 14:20	Plenary lecture - Norbert Jakubowski
14:20 - 14:40	Invited lecture - Johannes Van Elteren
14:40 - 15:40	Lecture session
15:40 - 17:30	Poster exhibition - Vendors exhibition
17:30 - 18:50	Lecture session
18:50 - 20:00	Vendors exhibition
19:00	Agilent Evening Event
20:00	Perkin Elmer Evening Event

FRIDAY, 24 FEB

SESSION 9 - APPLICATIONS AND FUTURE TRENDS

08:30 - 09:00	Plenary lecture - Gary Hieftje
09:00 - 09:20	Invited lecture - Olivier Donard
09:20 - 09:40	Invited lecture - Jörg Feldmann
09:40 - 10:50	Lecture session
10:50 - 11:20	Coffee break
11:20 - 13:30	Lecture session
13:30 - 14:00	Lunch break - Vendors exhibition LIGHT LUNCH SPONSORED BY ESI/Meinhard
14:00 - 16:00	Skiing race (Zielstadion)
14:00 - 19:00	Dismounting exhibition
17:50 - 22:00	Conference Dinner

Browse the complete programme directly from your phone or tablet and create your very own agenda on the fly.

3

ABSTRACTS

“Be less curious about people and more curious about ideas.”

– Marie Curie

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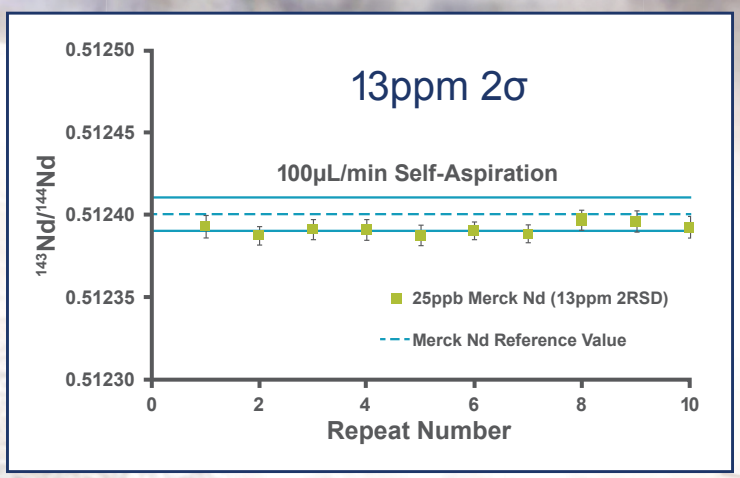
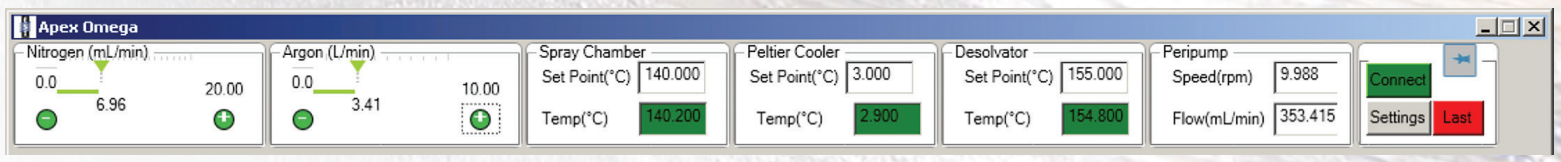


Full Software Control



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LECTURES

OPENING LECTURE: Opening lecture: SAM HOUK

Time: Sunday, 19/Feb/2017: 6:20pm - 7:20pm

Location: ARLBERG-well.com NORTH HALL

OPENING LECTURE: 1

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: ICP-MS, principles

MISNOMERS AND BAD TERMINOLOGY IN ICP SPECTROSCOPY

Sam Houk
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This talk will describe the overall status of ICP spectroscopy as a distinct scientific field. It has made many important contributions to scientific advances in other areas, but suffers from its own internal crisis, namely, the perception by others that there is not much left to do. One contribution to this issue is the fact that there are a number of common misunderstandings in the field, plus some poor terminology. Examples include the following:

1. ICP emission instruments are said to view the plasma radially, but in fact they view it with lateral resolution only.

2. ICP-MS instruments are said to do simultaneous multielement analysis, when almost all of them measure signals from various ions sequentially.

3. Various ICP-MS manufacturers use different terms to describe their means for removing polyatomic ions, when all these devices should be called merely collision cells. Even the journals have fallen for this one.

Lots more will come to mind by the time the talk rolls around.

FUN-PL 1: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - PLENARY LECTURE 1

Time: Monday, 20/Feb/2017: 8:30am - 9:00am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Gary M Hieftje

Session Chair: Florian Dutschke

8:30am - 9:00am

FUN-PL 1: 1

Topics: Glow discharge mass spectrometry, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Atmospheric-Pressure Glow Discharge, Mass Spectrometry, Direct Analysis, Ionization, Fragmentation

Unique Atmospheric-Pressure Plasmas: Understanding Ionization, Fragmentation, and Other Chemical Processes

Jacob T. Shelley[1], Sunil P. Badal[1], Andrew J. Schwartz[2], Courtney L. Walton[1], Kelsey L. Williams[3], Yi You[3], Garett M. MacLean[3], Gary M. Hieftje[2]

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Plasma ionization sources and mass spectrometry have gone hand-in-hand since J.J. Thomson first separated ions produced by a gaseous discharge over 100 years ago. Reduced-pressure plasmas were used as sampling/ionization tools for physical studies and analytical, atomic mass spectrometry. Later in the 20th century, the differentially pumped interface allowed the ion source to be external to the vacuum system, which simplified sample introduction for analytical purposes. Furthermore, the combination of this instrumental advancement with atmospheric-pressure plasma ionization sources offered a range of unique analytical capabilities. These atmospheric-pressure plasmas produce highly energetic species (*e.g.*, ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. This fragmentation can be so extensive that molecules are broken down into bare elemental constituents, as is the case in the inductively coupled plasma (ICP). In addition, low-energy ionization reactions can also occur due to the abundance of collisional cooling that can take place at ambient pressures, as is the case with corona discharges used for atmospheric-pressure chemical ionization. Thus, there are is a range of possible chemistries to be explored and understood.

This presentation will demonstrate the broad utility of low-power atmospheric-pressure glow discharges (APGD), specifically the flowing atmospheric-pressure afterglow (FAPA) and the solution-cathode glow discharge (SCGD). The possibilities of these devices extend well beyond conventional atomic and small molecule detection. By tuning the chemistry of the discharge, we can alter conventional ionization modes to encompass elemental analysis to biomolecular detection to polymer analysis. In one example, we have found the ionization pathway of the FAPA source to be highly tunable by changing plasma working conditions. Further, by slightly altering discharge-gas composition of the FAPA, the plasma can be used as a unique source of chemistry and can serve as reagent source for accelerated chemical reactions, which are known to have high potential-energy barriers. In another example, the SCGD was found to be capable of producing gas-phase ions of large, labile biomolecules directly from solution. Perhaps more surprisingly, the biomolecular ions can be controllably fragmented at atmospheric pressure through simple adjustment of the discharge parameters. The use of mass-spectral and optical data of these plasmas will be used to better understand the processes leading to ionization, fragmentation, and chemical rearrangement.

FUN-IL 1: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - INVITED LECTURES 1

Time: Monday, 20/Feb/2017: 9:00am - 9:20am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Gary M Hieftje

Session Chair: Florian Dutschke

9:00am - 9:20am

FUN-IL 1: 1

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: ICP-MS, modeling, Cu elemental particles, vaporization, ionization

ICP-MS: A better insight through computer modeling.

Annemie Bogaerts, Maryam Aghaei

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In this talk I will illustrate how computer modeling can contribute to a better insight in inductively coupled plasma – mass spectrometry (ICP-MS). I will explain the model that we developed in previous years, including the assumptions made, the equations to be solved and the input data and boundary conditions of the model. Our model simulates the ICP torch connected to a MS sampling cone, considering the large pressure drop from upstream to downstream (i.e. 1 atm to 1 torr). It describes the gas flow behavior inside the ICP, as well as typical plasma characteristics, such as plasma temperature and electron density. Besides, the effect of the injection of analyte material is accounted for. At this stage we focus on elemental particles, as relevant for LA-ICP-MS, but in a later stage, we want to extend the model to describe also the behavior of aerosols injected into the ICP. The inserted elemental particles are followed throughout the ICP, up to the evaporation step, and we also include ionization of the vapor atoms, taking Cu as a case study. The model allows us to trace the particles, and to determine their position, their phase (liquid, vapor or ionized), velocity and temperature, both in the ICP torch and at the sampler orifice. Thus, we can determine the shape and position of the ion clouds, originating from either the Ar flow or the inserted sample material, which is of interest for both OES and MS studies. Finally, we can obtain information on the fraction of Cu^+ ions passing the sampling cone, with respect to the amount of Cu injected into the ICP.

I will show typical calculation results, illustrating the plasma characteristics and gas flow patterns, as well as the sample transport, evaporation and ionization, to indicate what type of information can be obtained from the model, and how modeling can contribute to a better insight in the underlying mechanisms and help to improve the applications.

I will first show the general ICP characteristics and sample behavior at typical gas flow rates (i.e., 1 L/min injector gas, 0.4 L/min auxiliary gas, and 12 L/min outer gas flow rate), a plasma power of 1000 W, and Cu particles of 1 µm diameter, injected at a mass loading flow rate of 100 ng/s through an injector inlet of 1.5 mm diameter. Subsequantly, I will present the effect of the sampler orifice diameter and position, the injector inlet diameter and position of particle injection (including on-axis and off-axis injection), the gas flow rates and plasma power, as well as the particle diameter (in the range of 0.1 – 100 µm) and particle mass loading flow rate (in the range of 1 ng/s – 500 µg/s), on the ICP characteristics and on the behavior of the sample material, to illustrate how modeling can help to elucidate the optimal conditions for improved analytical performance.

FUN-OL 1: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - GENERAL SESSION 1

Time: Monday, 20/Feb/2017: 9:20am - 10:20am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Gary M Hieftje

Session Chair: Florian Dutschke

9:20am - 9:30am

FUN-OL 1: 1

Topics: Sample introduction and sample preparation, Elemental analysis, Plasma source fundamentals, instrumentation and mechanisms

Keywords: bioethanol, ethanol matrix effects, ICP-MS, ions distribution, hTISIS

Fundamental studies on the ions distribution in ICP-MS for ethanol-water matrices and its application to the determination of metals in bioethanol

Carlos Sánchez-Rodríguez[1], Charles-Philippe Lienemann[2], José-Luis Todolí-Torró[1]

[1]Department of Analytical Chemistry, Nutrition and Food Science. University of Alicante, Spain; [2]Analysis and Physics division. IFP Energies Nouvelles, France; carlos.sr@ua.es

The development of new analysis methods to determine metals and metalloids in bioethanol and other ethanol-water matrices is being developed recently due to the expansion of the biofuels.

Several methodologies have been employed successfully to carry out the quantification of metals in bioethanol-gasoline mixtures, called ethanol fuel.[1] However, a limited number of works have been focused in the determination of metals in pure bioethanol. The most important difficulty encountered to carry out the determination of metals in bioethanol is the huge variety of matrices under the called commercially as bioethanol, which can contain up to 7% of water and 300 different organic compounds, that causes matrix effects, thus requiring standard addition calibration. Recently, it has been reported the use of the total sample consumption system called hTISIS as a possibility to remove the matrix effects induced by ethanol in ICP-OES.[2] In this case, a single pass spray chamber has been heated at 400ºC. Under these conditions the analyte transport efficiency was the same for all the matrices studied. Nevertheless, when this introduction system was tested in ICP-MS under optimal conditions in terms of analyte transport efficiency, it was necessary to move the torch-interface alignment to fully remove the matrix effects. These observations suggested that the ions distribution in the plasma was dependent on the matrix composition and chamber temperature.

In the present work, axial and radial plasma ionic profiles have been obtained for several analyte isotopes and additional diagnostic magnitudes such as CeO^+/Ce^+ and Ce^{++}/Ce^+ ratios and background ions. The hTISIS has been employed so as to remove interferences arising in the aerosol transport step. An ICP-MS Agilent 7700x equipped with a High Matrix Introduction device (HMI) and a He collision cell has been used. The signal profiles have been obtained for different injector inner diameters, hTISIS temperatures; 1st and 2nd extraction lens voltages and ethanol concentrations.

The data generated in the present work revealed the capital importance of the torch injector inner diameter and the spectrometer plasma sampling zone. These results allow to better understand the interferences caused by ethanol in ICP-MS and they have been applied to the determination of metals and metalloids in bioethanol samples by means of the external calibration under optimal conditions of matrix effects and sensitivity.

References.

[1] Metal and metalloid determination in biodiesel and bioethanol, Raquel Sánchez, Carlos Sánchez, Charles-Philippe Lienemann, José-Luis Todolí,J. Anal. At. Spectrom., 30 (2015) 64-101.

[2] Metal and metalloid determination in bioethanol through inductively coupled plasma-optical emission spectroscopy, Carlos Sánchez, Charles Philippe-Lienemann, José-Luis Todolí, Spectrochimica Acta Part B 115 (2016) 16–22.

9:30am - 9:40am

FUN-OL 1: 2

Topics: Sample introduction and sample preparation, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: laser ablation, flowing atmospheric pressure afterglow, mass-spectral imaging

Coupling of laser ablation with halo-flowing atmospheric pressure afterglow-mass spectrometry as a new molecular imaging technique

Valérie Anne Brückel[1], Uwe Karst[1], Michael Sperling[1,2], Jacob T. Shelley[3]

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Coupling of Laser Ablation with halo-Flowing Atmospheric-Pressure Afterglow-Mass Spectrometry as a New Molecular Imaging Technique

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Mass-spectral imaging (MSI) has become a valuable tool for the measurement of spatial distributions of target analytes in complex samples. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is the method of choice in order to investigate elemental distributions particularly due to the high spatial resolution, minimal sample preparation, and excellent sensitivity offered by this combination. While MSI of molecular species is often performed with matrix-assisted laser desorption/ionization (MALDI) and secondary ion mass spectrometry (SIMS). Due to the requirements of these methods, molecular MSI is reliant upon a cumbersome sample preparation, partly due to the fact that the sample is analyzed in the vacuum of the mass spectrometer.

The difficulties of mass-spectral analysis that arise from the necessity of introducing the sample into the vacuum of the mass spectrometer led to the development of ambient desorption/ionization mass spectrometry (ADI-MS) in the past decade. In 2013, Pfeuffer *et al.* introduced a new ADI-MS source called halo-flowing atmospheric pressure afterglow (halo-FAPA).[1] Here, molecules are desorbed/ionized in the afterglow region of a halo-shaped atmospheric pressure glow discharge sustained in helium. Due to the ionization chemistry of halo-FAPA-MS, molecules of a broad range of polarities in the relatively low mass range (*e.g.*, under 1000 Da) can be detected at very low amounts (*ca.* 100 amol).

In this work, a new molecular MSI technique is presented. It is based on coupling of LA with FAPA-MS. This technique overcomes the difficulties of sample preparation encountered with MALDI or SIMS by allowing the sample to be ablated and analytes to be desorbed/ionized under ambient conditions. The coupling of halo-FAPA-MS with LA enables the combination of the high spatial resolution in the tens of micrometers and good reproducibility of the sample introduction provided by the LA unit with the distinct advantages of the FAPA ion source, which include a high sensitivity for molecular analytes. In addition, the FAPA source can easily be coupled with different mass analyzers, allowing the use of either high-resolution MS or tandem-MS in order to enhance chemical selectivity.

[1] K. P. Pfeuffer, J. N. Schaper, J. T. Shelley, S. J. Ray, G. C.-Y. Chan, N. H. Bings, G. M. Hieftje, *Anal. Chem.* **2013**, *85*, 7512–7518.

9:40am - 9:50am

FUN-OL 1: 3

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: Plasma fundamentals, discret sample introduction, droplets, nanoparticles

Fundamental plasma investigation using microdroplets with ICP-TOFMS

Lyndsey Hendriks, Alexander Gundlach-Graham, Detlef Günther

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For a range of emerging applications, such as single-nanoparticle analysis, one must measure mass-limited discrete signals, so that detection efficiency (counts/atom entering plasma) is a limiting factor. Detection efficiency depends on various interactions and processes between the sample, analyte, and the plasma, such as sample desolvation, vaporization, atomization, ionization and ion sampling. Hence, a better understanding of the relative significance of these processes on detection efficiency, to which a particular droplet or particle is subjected to in the ICP, is an important prerequisite for improving the accuracy in the analysis of single entities, such as microdroplets, nanoparticles, and single cells.

To gain better insight into plasma fundamentals, microdroplets were used to investigate plasma-sample interactions. We combined a newly developed ICP-TOFMS (*icp*TOF, TOFWERK) instrument with a microdroplet generator (Microdrop Technologies GmbH) for discrete sample introduction into the ICP. Monodisperse droplets were produced on-axis to the ICP and introduced into the plasma via a stream of helium and argon gas to focus their trajectories and partially dry them[1]. Thanks to the narrow size distribution of the droplets, the time required to undergo desolvation, atomization, and ionization in the ICP is highly reproducible from one droplet to another, which makes this sample introduction system an ideal tool for investigating fundamental ICP processes[2]. Using the TOFMS, we recorded complete elemental spectra from individual microdroplets at a time resolution of 30 µs in order to examine the composition and signal structure from individual droplets. Specifically, we measured the dependence of sensitivities for different multi-element solutions on the time the droplet/analyte spend in the plasma, by varying the sampling position. For low concentrations (10–100 ng/g), signal intensity was recorded over a sampling depths from 2–8 mm and decreased due to ion diffusion in the plasma. However, for higher concentrations, sampling depth more strongly affected sensitivity; with a 1000 ng/g solution, signal was not even detected until a sampling depth of 4 mm and diffusion dominated sensitivity loss after 6 mm. Additionally, robust plasma conditions were obtained only at concentration dependent sampling depths. These preliminary experiments have lead us to question the influence of particle size on ionization in the ICP and to investigate the effects of analyte mass and plasma loading for multi-elemental detection from individual droplets. Because microdroplets serve as a proxy for nanoparticles, this study also has implications for the accurate sizing of nanoparticles, single cells…

[1] (a) Gschwind, S. et al, *Anal Chem* **2013,** *85* (12), 5875-5883; (b) Borovinskaya, O. et al, *Anal Chem* **2014,** *86* (16), 8142-8148.

[2] (a) Olesik, J. W. *Appl Spectrosc* **1997,** *51* (5), A158-A175; (b) Borovinskaya, O. et al, *J Anal Atom Spectrom* **2014,** *29* (2), 262-271.

9:50am - 10:00am

FUN-OL 1: 4

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: ICP-MS, Laser ablation, Computational study, Transport efficiency

Formation, tracking and transport of ion clouds in the inductively coupled plasma torch: a focus on brass components

Maryam Aghaei, Annemie Bogaerts

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A self-consistent model for an atmospheric pressure inductively coupled plasma (ICP), operating at typical analytical chemistry conditions, is presented. The model is based on solving partial differential equations for the gas flow dynamics coupled with the energy conservation and Maxwell equations. The power coupling is a source term in the energy conservation equation, whereas the emitted radiation is a loss term. The electromagnetic fields, the amount of ionization, as well as the material parameters, i.e., electrical conductivity, viscosity, heat capacity, thermal conductivity and diffusion coefficients as a function of the actual gas composition and plasma temperature are calculated by some self-written codes. This makes it possible to apply the model to a wide variety of gas mixtures, including carrier gas and sample material. Typical calculation results from the model include the gas flow behavior, as well as the plasma temperature and electron density profiles [1-4].

The model includes the introduction of elemental particles, which is relevant for “laser ablation” ICP-MS, where the sample is injected as ablated elemental particles [5]. The trajectory of each droplet is calculated by integrating the force balance acting on the particles. The heat lost or gained by the particle will also appear as a source or sink in the energy equation. From the ionization degree and the mass and charge conservation equations, the number densities of electrons and of the atoms and ions of the sample material are calculated.

This model enables us to track the particles to determine their position, their phase, velocity and temperature both in the ICP torch and at the sampler orifice [6]. By integrating the number density of ions passing through the sampler over the orifice width and the torch exhausts, and comparing to the entering material, we calculate the transport efficiency at different conditions and we explain the whys behind it.

Specifically, the behavior of brass components, i.e., copper and zinc at different fractions, is studied. Indeed, due to different boiling and ionization temperatures, as well as the different viscosity and diffusion coefficients of different materials, the position at which the sample or sample cloud may move in the radial direction to the outer region and become further away from the central channel is different. Hence, this enables us to learn to what extent these differences affect the ion cloud transport towards the sampler cone.

[1] M. Aghaei, H. Lindner and A. Bogaerts, *J. Anal. At. Spectrom.,* **27**, 604, 2012

[2] M. Aghaei, H. Lindner and A. Bogaerts, *Spectrochim. Acta Part B,* **76**, 56, 2012

[3] M. Aghaei, H. Lindner and A. Bogaerts, *J. Anal. At. Spectrom.,* **28**, 1484, 2013

[4] M. Aghaei, L. Flamigni, H. Lindner, D. Gunther and A. Bogaerts, *J. Anal. At. Spectrom.*, **29**, 249, 2014

[5] M. Aghaei, A. Bogaerts, *J. Anal. At. Spectrom.*, **31**, 631, 2016

[6] M. Aghaei, H. Lindner, A. Bogaerts*, Anal. Chem.*, DOI: 10.1021/acs.analchem.6b01189

10:00am - 10:10am

FUN-OL 1: 5

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: multi collector mass spectrometer, ICP, EBIS

Multiple ion source multi collector mass spectrometer

Niko Kivel, Heiko-Dirk Potthast, Matthias Martin
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In the recent past the mass discrimination in MC-ICP-MS was investigated by a multitude of researchers. However, the comparability of the findings is complicated by the fact that different types of mass spectrometers were used in these studies. Since the mass discrimination is most likely dominated by the ion source, or the extraction of the ion from the source it is proposed to adapt different sources to one mass spectrometer only. With this approach the impact of the subsequent mass spectrometer can be ruled out completely.

The proposed device will incorporate an ICP source as manufactured by the vendor. With a modification of the ion optics the device will be modified to accommodate additional ion sources and beam diagnostics. In the first step an electron beam ion source (EBIS) will be adapted. This source is able to deliver high ion currents with very high stability. Additionally the EBIS is able to produce highly charged ions up to He-like states for most elements with Z <= 54.

The presentation will cover the fundamental aspects of the proposed instrument. Furthermore the results of preliminary design studies for the ion optics and beam guidance system will be presented. In an outlook the ability to harness further ion sources to the mass spectrometer will be demonstrated.

10:10am - 10:20am

FUN-OL 1: 6

Topics: Elemental analysis, Plasma source fundamentals, instrumentation and mechanisms
Keywords: attenuation mode, ICP-OES, elemental analysis

Benefits and Applicability of Attenuation Mode for ICP-OES Analyses

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With ever-increasing demands being made on analytical instrumentation to measure lower analyte levels, it is easy to forget about the analyses which require accurate measurements at high concentrations. Due to its high matrix tolerance, wide dynamic range, and multi-elemental capabilities, ICP-OES can be an ideal technique to measure high concentrations of inorganic elements. Typically, for samples with extremely high elemental concentrations, the dynamic range of ICP-OES instrumentation will be extended by changing the viewing mode and picking less sensitive alternate wavelengths. However, if the instrument has the capability, another option is to run in attenuation mode where the intensity of user-selected wavelengths can be attenuated without affecting the intensity of the remaining wavelengths of interest. Attenuation mode relieves the operator of having to evaluate multiple alternate wavelengths for potential interferences, switching the plasma view, or excessively diluting the samples which can affect sample homogeneity, pH, and accuracy. As a result, attenuation mode is particularly useful when measuring samples that contain both high and low concentrations of the elements of interest. This work will discuss attenuation mode and show practical examples of its use in ICP-OES analyses.

FUN-OL 2: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - GENERAL SESSION 2

Time: Monday, 20/Feb/2017: 11:00am - 12:20pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Gary M Hieftje

Session Chair: Florian Dutschke

11:00am - 11:10am

FUN-OL 2: 1

Topics: Sample introduction and sample preparation, Elemental analysis

Keywords: Gold, REE, geochemical, alkali fusion, ICP-MS

Enhanced sensitivity ICP-MS for routine analysis of geochemical samples by alkali fusion

Lou Daniel[1], Andrew Jason Ryan[2], Rui Santos[2]

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An Analytik-Jena, PlasmaQuant Elite ICPMS has been applied to direct analysis of gold and rare earth elements (REE) in high TDS solutions obtained by fusion of geochemical certified reference materials (CRM) with sodium peroxide + sodium hydroxide mixtures. The fusion procedure is simple, fast and designed for application to high throughput commercial laboratories. A loop injection system was used to provide a fully inert sample introduction path and to thereby avoid long washout times otherwise required for gold analysis. Accurate results were obtained for Au, using sample weights of up to 25 g, and REE in CRM with a wide range of composition. Ground breaking sensitivity was obtained with limits of detection, on an analyte-in-CRM basis, of 0.01 ppm Au and ≤ 0.01 ppm for REE. This is an order of magnitude improvement upon previously reported performance of geochemical analysis by alkali fusions. In the case of Au analysis, where larger sample weights are generally used to overcome heterogeneity in samples, this suggests a practical alternative to the problematic procedure of fire assay for Au using lead oxide. In the case of REE, this simple and inexpensive procedure matched or exceeded the sensitivity of elaborate and expensive hybrid acid digestion + lithium borate fusion methods currently used commercially to obtain these detection limits.

11:10am - 11:20am

FUN-OL 2: 2

Topics: Sample introduction and sample preparation
Keywords: undiluted, fuel, gasoline, silicon, POINT

Direct Undiluted Analysis of Fuels by ICP with POINT Organic Aerosol Sample Introduction System

Gerhard Meyer
Promerus LLC, United States of America; gary.meyer@promerus.com

The aerosol from organic solvents ranging in vapor pressures from 9 to 70 kPa (compared with vp for water of 3 kPa at 23C) can be easily introduced undiluted into an argon ICP using a simple combination of a high efficiency nebulizer (HEN, Meinhard Elemental Scientific Glassblowing LLC) and a special 2 cc internal volume microspray chamber (POINT, Meinhard Elemental Scientific Glassblowing LLC). The temperature inside the 2 cc transfer chamber during nebulization of highly volatile organic solvents has been reported to be well below 0 degrees Celcius which precludes needing any external cooling of the chamber. Fuels such as gasoline and diesel can be easily anlayzed undiluted using this method. Flow rates are typically around 200 microliters per minute or less at argon gas flow rates of 3 LPM. Performance characteristics and operating conditions for the determination of Si and other metals in gasoline at parts per billion levels by ICPOES and ICPMS will be presented.

11:20am - 11:30am

FUN-OL 2: 3

Topics: Sample introduction and sample preparation, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: dbdi, laser desorption, mass spectrometry, plasma gas mixture, soft ionization

Argon-propane plasma for ionization of laser desorbed molecules

Alexander Schütz, Sebastian Brandt, Felix David Klute, Joachim Franzke

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The first time a dielectric barrier discharge ionization (DBDI) was coupled to mass spectrometry (MS) is about 10 years ago when the DBDI source was used for desorption and ionization simultaneously. While the separation of desorption and ionization has some advantages, the sample introduction is still a challenge. The ionization of gaseous and low volatile compounds can be done with low effort but an advancement for liquid and solid non-volatile compounds can be realized by laser desorption (LD).

Here, a nondestructive method for lifting molecules from a surface (desorption) is presented. Therefore diverse laser with different wavelength were used, while this technique needs no matrix but a post ionization. Dependent on the wavelength the desorption process is based on a fast heating of a surface (cw 450 nm, cw 808 nm) or on a direct excitation of OH-bands (pulsed 2940 nm). Because of the following transportation system, a low laser power and fluence was used to prevent the generation ions. Thus, it differs from common techniques like matrix assisted laser desorption/ionization (MALDI) and surface assisted laser desorption/ionization (SALDI).

Since a square-wave high-voltage is used to operate the DBD, the change of the duty cycle allows to switch on or off the dissociative part of the plasma. This offers a novel opportunity to use the same ion source for the detection of elements e.g. by optical emission spectroscopy (OES) or for soft ionization for organic mass spectrometry. Until now helium was used as plasma gas because of its low ignition voltage and ionization efficiency. Therefore, the analyte has to be vaporized by laser desorption and transported into the plasma jet under ambient conditions. The use of an argon-propane mixture enables a lower ignition voltage for the plasma in argon and allows to operate a gastight system. Furthermore, with the prevention of the dissociative plasma, the analyte can be transported through the discharge capillary instead of an introduction at ambient conditions. This is due to the fact that for the ionization by excited Argon nitrogen is no longer necessary.

Because of its modular structure, all single parts (sample preparation, desorption, transport, sample introduction, ionization and detection) can be studied individually. Some advantages over common atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) will be presented.

Finally, the experiment can be extended with in-house build accessories like a 3d-printed auto sampler or controlled by single-board computers like the Raspberry Pi or Red Pitaya easily.

11:30am - 11:40am

FUN-OL 2: 4

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: Beam homogenization and delivery by two-stage Fourier Optical Processing

Femtosecond laser ablation ICPMS: Beam delivery by two-stage Fourier transform optical processing for high resolution depth profiling of metal layers

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Ultraviolet nanosecond (UV-ns) laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) has become an off-the-shelf technique for the analysis of major, minor, and trace elements in diverse fields of research such as geology or material science. In recent years, the feasibilities of near infrared (NIR) and UV femtosecond (fs) laser sources have been studied to improve the accuracy and precision of LA-ICPMS analyses [1, 2] and, thus, to broaden the range of applications. However, little progress has been made to increase the *depth resolution* of fs-LA-ICPMS primarily given by the degree of homogenization of the radiation´s intensity profile across the target surface and the mean up-take rate per laser shot. The delivery of homogenized fs laser radiation at ambient pressures has been challenging until today since conventional optical set-ups used, *e.g.*, in ns-LA [3] were found to be hardly applicable unless pulse energies are kept low. The difficulty of delivering homogenized fs laser radiation originates from high peak intensities above 10^{13} W/cm^2 around intermediate focal planes, which often results in a distortion of the intensity profile along the beam path and, thus, the formation of misshapen craters. Still, there is a need for alternative and versatile homogenization concepts to push the depth resolution closer to the ultimate limit determined by up-take rates of less than about 10 nm per laser shot [4].

This paper is dealing with the beam delivery by two-stage Fourier transform (TSFT) optical processing: First, the laser beam was truncated by a circular aperture to let pass only the inner region of a Gaussian raw beam, where radial intensity gradients were smallest and, thus, the uniformity was highest. Through truncation, the beam was diffracted to form an Airy disk in the far field of the aperture (1st FT). Subsequently, the Airy disk was focused by an aberration-corrected lens, acting as the second Fourier optical processor (2nd FT). The performance of this scheme was tested on a chirped pulse amplification (CPA) Ti:Al_2O_3 fs laser system operated at a wavelength of 400 nm for LA under ambient condition, helium atmosphere, and vacuum. Surface morphology studies carried out on metals and insulators by optical microscopy, scanning electron microscopy, and atomic force microscopy revealed the formation of well-shaped craters with flat bottoms and steep walls. Further, depth profile analyses of both pure Cr and alternating Cr/Ni layers by TSTF-fs-LA-ICPMS gave up-take rates of <7.5nm per laser shot whereas depth resolutions were in a range <500nm, depending on the over-all thickness of layers. Mechanisms defining the depth resolution achievable by TSTF-fs-LA-ICP-MS of metal layers are discussed.

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11:40am - 11:50am

FUN-OL 2: 5

Topics: Sample introduction and sample preparation, Elemental analysis
Keywords: VAMS, ICP-MS/MS, tandem mass spectrometry, whole blood

Determination of ultra-trace amounts of prosthesis-related metals in whole blood using volumetric absorptive micro-sampling and tandem ICP – Mass Spectrometry

Lieve Balcaen[1], Eduardo Bolea-Fernandez[1], Kim Phan[1], Martín Resano[2], Frank Vanhaecke[1]
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The development of accurate and sensitive analytical methods for the determination of (ultra)trace elements in human blood has been the subject of many studies over the years, not only in terms of analysis, but also in terms of sample collection, sample conservation and sample preparation.

Next to the most common venipuncture method, also the use of dry sampling methods, such as the collection of dried blood spots (DBS), and, more recently, volumetric absorptive micro-sampling (VAMS) came into the pharmaceutical and medical community, because of their inherent advantages (minimally invasive, improved sample conservation and easier transport of samples to the laboratory).
Due to the increasing use of metal-based implants and the concern about metal release into the body by degradation and/or malfunctioning of these implants, regular monitoring of the blood trace element composition of implanted patients is required. This necessitates efficient, fast and trustworthy analytical approaches for the determination of (ultra)trace amounts of various prosthesis-related metals (e.g., Al, Ti, V, Cr, Co, Ni, Sr and Zn) in biofluids. While the most recent dry sampling method – VAMS – has proven successful for bioanalysis (especially in the context of drug analysis and pharmacokinetics), no work had reported on the use of VAMS with the aim of (ultra)trace element analysis.

In this work, a simple dilute-and-shoot approach (100-fold dilution) followed by tandem ICP-mass spectrometry (ICP-MS/MS) analysis was developed for the accurate and sensitive determination of the target elements. The ICP-MS/MS method relies on the use of mass shift reactions proceeding when pressurizing the collision/reaction cell (CRC) with CH_3F/He to deal with spectral overlap. Limits of detection (LoDs) between 0.3 and 30 ng L^{-1} were attained in a multi-element approach. The accuracy of the method was demonstrated *via* successful analysis of the reference materials Seronorm Whole Blood Levels 1 and 3, and real venous blood samples, spiked with the target elements at different concentration levels (5–50 µg L^{-1}). Although the implementation of VAMS devices introduced contamination problems for Al, Cr and Ni, VAMS followed by ICP-MS/MS analysis shows potential for future real-life routine applications when assessing levels of Ti, V, Co, Sr and/or Zr.

11:50am - 12:00pm

FUN-OL 2: 6

Topics: Elemental analysis

Keywords: Single cell analysis, Human cell analysis, Trace elemental analysis, ICP-AES/MS

High-sensitive Elemental Analysis of Single Human Cell using Droplet Injection ICP-AES/MS

Takahiro Iwai[1], Shunsuke Hosoda[2], Satoshi Kohno[2], Mari Aida[2], Ken Kakegawa[2], Tomoko Miyake[2], Hidekazu Miyahara[2], Yoshihisa Matsumoto[3], Koichi Chiba[1], Akitoshi Okino[2]

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Trace element analysis in a single cell has been expected to contribute in the clarification of biological activities such as differentiation process of iPS cell and pathogenesis of cancer. To analyze trace elements in a single cell of ppb level, introduction of individual cell into analytical instruments and ag (10^{-18} g) level analytical sensitivity are required. In our previous researches, Droplet Direct Injection Nebulizer (D-DIN)[1-3], which can introduce sample solution into Inductively Coupled Plasma (ICP) as a single droplet of 14 to 180 pL volume, and a desolvation system for D-DIN[4] heve been developed. Using these systems, limit of detection at ag level was achieved by introducing 14 pL droplet of Pb standard solution (0.1 µg/L) to ICP Mass Spectrometer (ICP-MS). Furthermore, a single droplet which contains a single cell of unicellular algae (*pseudococcomyxa simplex*) was introduced to ICP and multi-element analysis of Ca, Mg and Fe, whose amounts were approximately 11, 57 and 80 fg in a single cell, respectively, were achieved.

In this study, trace elements in a single human cell were measured by D-DIN and ICP analytical system. Human cervical carcinoma HeLa and osteosarcoma U2OS cells were used as the samples. Before analyzing a single cell, human cell samples were decomposed in a mixed-acid solution and analyzed by conventional analytical method using ICP-MS to know the average amount of metallic elements contained in the cells. Then, D-DIN system was applied to ICP-AES for multi-element single cell analysis. As the result, emission spectra of Ca and Mg, whose amounts were pg level in single human cell, were successfully detected simultaneously.

For higher sensitive analysis, single cell analysis by D-DIN-ICP-MS was investigated. First, uniform-sized particles of magnetic polymer latex were analyzed by D-DIN-ICP-MS for evaluating precision of the system. The mass signal of Fe from the particles was measured directly from the ion detector using a digital oscilloscope with high sampling rate for improving the time resolution. As the result, RSD of the measurement achieved by this system was 42%. Then, a single droplet containing a single human cell was introduced to ICP-MS (7500ce Agilent Technologies). The distribution of trace element content in each of the cells was evaluated from variations of the mass signal intensity and the RSD estimated by the analytical system.

1. Shigeta *et al.*, *J. Anal. At. Spectrom.,* **2013**, *28,* 646.
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12:00pm - 12:10pm

FUN-OL 2: 7

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: soft ionization, DBDI, homogeneos discharge

Soft Ionization by a homogeneous plasma or when plasma and ionization place are separated?

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Dielectric barrier discharges are used for analytical applications as dissociative source for optical emission spectrometry and for ambient-ionization techniques. In the range of ambient-ionization techniques it has attracted much attention in fields like food safety, biological analysis, mass spectrometry for reaction monitoring and imaging forensic identification. The dielectric barrier discharge cannot only be used as desorption and subsequent ionization source but also as soft ionization source for different sample introductions solely.

According to Kogelschatz at least one dielectric layer has to be in between the electrodes when it is called dielectric barrier discharge [1]. A dielectric barrier discharge with just one dielectric layer is formed by a pin-ring or a tube-ring-shape. In most cases an ac-high voltage is applied at the ring electrode which is wrapped around the capillary while the electrode inside the capillary (pin or tube) is grounded. This polarity is preferred in order to avoid a direct plasma in between the pin or tube-electrode to a possible grounded surface when the pin or tube-electrode would be contacted to the ac-high voltage. In general dielectric barrier discharges generated with only one dielectric barrier and sinusoidal voltages are based on the separation of the ionization area and the discharge area.

There were ionization sources which were modified consecutively by separating more parts of the plasma from the place where the analyte is introduced resulting in a configuration called double cylindrical discharge tube [2]. In the case of the active capillary ionization source even the use of noble gases could be avoided resulting in extraordinary LODs for chemical warfare agents [3].

When dielectric barrier discharges are used which are based on the ring-ring shape with two dielectric barriers and when these are operated in a homogeneous mode the analyte can be introduced directly into the soft plasma. Due to spatio-temporal measurements it could be shown that the ring-ring shape plasma consists of several plasmas: plasma jet, inner early plasma, and coincident plasma which is capable of dissociating molecules [4, 5]. This is the reason why analytes which should exclusively be ionized softly avoiding fragmentation are introduced into the plasma jet and not fed in the capillary together with the discharge gas.

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12:10pm - 12:20pm

FUN-OL 2: 8

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: Ambient Desorption/Ionization Mass Spectrometry, Liquid Crystal Display

LIQUID CRYSTAL DISPLAY SURFACE ANALYSIS FOR FAST DISPLAY FAILURE INVESTIGATION BY AMBIENT DESORPTION/IONIZATION MASS SPECTROMETRY

Christopher Kuhlmann[1], Sunil P. Badal[2], Jacob T. Shelley[2], Carsten Engelhard[1]
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Liquid crystal displays (LCDs) are one of the most commonly used display technologies worldwide. Quality control, particularly for monitoring/understating display failure, as well as further product development necessitates powerful analytical methods to rapidly analyze these complex materials. Chromatographic techniques coupled to mass spectrometry and microscopy methods are typically used for liquid-crystal analysis. Because these methods, and the associated sample pretreatment steps (*e.g.*, manual extraction of liquid crystals (LCs) from a large-format display), are very time consuming and require appreciable amount of solvent, there is a need for alternative greener methods to increase sample throughput. Ambient desorption/ionization mass spectrometry (ADI-MS), a rapidly emerging field of organic mass spectrometry, is well suited for such a task because it can be used to directly desorb and ionize analytes from the sample surface with minimal sample preparation or consumption of solvent. The ions are then transferred through the vacuum interface of the mass spectrometer to the mass analyzer region via the instrument's ion optics. Sample analysis times, including preparation steps, can be on the order of a few seconds with these ADI-MS methods.

In this study, selected plasma-based ADI sources, direct analysis in real time (DART) [1], flowing atmospheric-pressure afterglow (FAPA) [2], and low-temperature plasma (LTP) [3], will be compared for the direct analysis of liquid-crystalline materials by mass spectrometry. The main aim of this work is to minimize sample preparation for quick and cheap LCD failure analysis by differentiating between liquid crystals and corresponding degradation products inside the device. Additionally, further improvements in mass-spectral imaging of LCDs will be presented. In the present case, imaging is performed with laser ablation (LA) coupled to FAPA-MS. Localized samples of liquid crystalline material was removed from the solid substrate with a focused laser beam. The ablated material was ionized by a FAPA source. This instrumental setup enables the analysis of very low sample volumes that are present inside the LCD. Ultimately, this method shall help to differentiate between different LCD components and identify defects within a LCD by lateral profiling.

References:

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FUN-IL 2: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - INVITED LECTURES 2

Time: Monday, 20/Feb/2017: 1:40pm - 2:20pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Jacob Shelley

Session Chair: Tristan Zimmermann

1:40pm - 2:00pm

FUN-IL 2: 1

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: inductively coupled plasma, microdroplet, plasma perturbation

How does an ICP respond to the introduction of a single micro-droplet? (SPECTROSCOPY MAGAZINE AWARD LECTURE)

George Chan[1,2]

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Elemental analysis of single particles (sp) with the inductively coupled plasma (ICP) is conceptually straightforward with the use of a monodisperse microdroplet dispenser. The individual entities (e.g., nanoparticles or biological cells) to be measured are embedded inside solution droplets, which are then introduced into the ICP. Ideally, each such droplet contains no more than a single particle, and the analytical signals from individual entities are well separated in time and can be registered in the form of discrete signal spikes. Because of the monodisperse size distribution of the droplets, the time (which translates into height in the plasma) required for the droplet to undergo complete desolvation, atomization, excitation and ionization is very reproducible from droplet to droplet, and it then becomes possible to predict the arrival time of the signal spike.

Motivated by the recent growing interest in nanoparticle analysis with sp-ICP spectrometry, which creates a new demand for a better fundamental understanding of the ICP, we monitored the physical behavior of the ICP during single-droplet introduction. We observed that droplet introduction perturbed the plasma in a way that involved three sequential effects: local cooling, thermal pinching and plasma reheating. In this presentation, the momentary changes in plasma characteristics caused by introduction of a single micrometer-sized droplet will be described and discussed.

2:00pm - 2:20pm

FUN-IL 2: 2

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: Atomic Mass Spectrometry, Instrumentation

Distance-of-Flight Mass Spectrometry for Atomic Anlayses: Latest Results

Steven James Ray[1], Gary Hieftje[2], Chris Enke[3], David Koppenaal[4]

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Inductively-coupled plasma mass spectrometry (ICP-MS) is a vanguard analytical technique, however, new instrumental approaches can unlock even more significant capabilities. Here, a new type of mass analyzer known as the distance-of-flight mass spectrometer (DOFMS) will be evaluated for ICP-MS. The DOFMS concept is best explained by comparison with traditional time-of-flight mass spectrometry (TOFMS). TOFMS measures the mass-to-charge (*m/z*) of an ion by imparting the same energy to all ions and then measuring the time required for each *m/z* to traverse a distance and arrive at a single detector. In contrast, DOFMS measures the *m/z* of an ion by measuring the distance each ion travels during a set time period. Simply put, ions of lower *m/z* traveling longer distances than ions of greater *m/z*, and their *m/z* can be determined based upon location.

The DOFMS strategy offers a number of significant benefits for ICP-MS. Like TOFMS, DOFMS is architecturally simple, offers very rapid spectral generation rates, and is capable of simultaneous multielemental analysis. However, DOFMS is able to employ new solid-state array ion detectors to great advantage, providing greater detection efficiency and dynamic range than typical TOFMS, and obviating the need for fast electronics. As important, the DOFMS strategy permits new experiments to be performed. For example, DOFMS focusing strategies can be employed in a typical TOFMS experiment to improve mass resolution over a limited window of the atomic mass spectrum. This technique, known as Zoom-TOFMS, is able to increase mass resolution while simultaneously increasing the S/N of the mass spectrum. Moreover, because TOFMS and DOFMS share a common architecture, a single instrument is able to switch between TOFMS, DOFMS, and Zoom-TOFMS experiments as required. The theory of operation and experimental advantages of DOFMS will be discussed, and the analytical performance of this new type of mass spectrometer will be described.

FUN-OL 3: FUNDAMENTALS OF PLASMA SPECTROCHEMISTRY - GENERAL SESSION 3

Time: Monday, 20/Feb/2017: 2:20pm - 3:30pm
Location: ARLBERG-well.com NORTH HALL
Session Chair: Jacob Shelley
Session Chair: Tristan Zimmermann

2:20pm - 2:30pm

FUN-OL 3: 1

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: DBD, OES, dissociation, soft ionization

Spatio-temporal development of a dielectric barrier discharge for analytical applications

Felix David Klute, Sebastian Burhenn, Antje Michels, Sebastian Brandt, Alexander Schütz, Joachim Franzke
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Dielectric barrier discharges (DBD) are suitable for both soft ionization and dissociation of molecules. Due to their simple design, the capillary DBD provides easy accessibility for optical diagnostics, such as optical emission spectroscopy (OES). By observing the temporal and spatial generation of relevant species in the plasma it was shown that the mechanisms responsible for soft ionization and dissociation, are temporally and spatially separated. To this end, the temporal evolution of the spectral lines of the most important components in the plasma, namely He* 706 nm, N_2^+ 391 nm and O 777 nm, representing exited species of the working gas, ions, and dissociated and exited species was measured at certain positions along the discharge axis. It could be shown that the processes responsible for soft ionization are early located in the external plasma-jet whereas the dissociation takes place late in the plasma within the capillary. Therefore, by means of a suitable electrical setup it is possible to suppress the dissociative plasma and enhance soft ionization. On the other hand an increase of the power coupled into the plasma enhances its dissociative character. This can be achieved by optimizing the electrode geometry resulting in a higher amount of charges fed into the discharge. The dissociative capability of the capillary DBDI is demonstrated with several analytes such as $CHClF_2$ and $CHCl_3$ yielding in absolute detection limits in the range of 10 – 100 pg.

2:30pm - 2:40pm

FUN-OL 3: 2

Topics: Nanomaterials, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Single Particle ICP-MS, Nanoparticles

Advancement in Single Particle ICP-MS – Significant Instrument Settings and their Implications on data Quality

Chady Stephan, Hamid Badiei, Samad Bazargan, Aaron Hineman
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The characterization, sizing, and quantification of metal-based nanoparticles (NP) in a variety of matrices using single particle-inductively coupled plasma-mass spectrometry (SP-ICP-MS) is becoming increasingly popular due to the sensitive nature of the technique. Novel reaction cell optimizations, instrument settings, and data processing techniques are used to explore the benefits of continuous data acquisition rates as fast as 10^5 Hz (or 10 µs dwell times).

This talk presents data on the various significant instrument settings and their implications on nanoparticle characterization. Information on instrument setup, sample prep and transport efficiency on data quality is given. The effect of varying the dwell time and its influence on particle integration, particle counting, particle sizing, and background signal is discussed. Data describing the use of Dynamic Reaction Cell (DRC) design in handling short-lived transient events while managing spectral interferences is also introduced.

2:40pm - 2:50pm

FUN-OL 3: 3

Topics: Nanomaterials

Keywords: sp-ICP-MS, Signal processing, microsecond dwell time, background determination, peak detection

A robust signal processing approach for single particle-ICP-MS analysis with dwell times in both the millisecond and microsecond range

Samad Bazargan, Hamid Badiei

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Improvements in the data acquisition rate of ICP-MS instruments have made it possible to capture the transient signal generated by the ion clouds of individual nanoparticles. This transient signal can be detected and then quantified against calibration standards in order to gain information about the size, concentration, and composition of the nanoparticles. Decreasing the dwell time of measurement for such analyses to as low as 100µs-10µs improves the detection of adjacent nanoparticle events, and makes it possible to distinguish between the signal associated with the nanoparticle event and the steady background, particularly in the case of interfered analytes. This however poses a challenge in processing the data as the total signal of the event is distributed among multiple measurement points. Once the dissolve or the steady state background is determined, these multiple points need to be detected as a single nanoparticle event, and their contribution should be summed up to obtain the total signal per event. In this talk, we focus on this challenge and present the signal processing approach that we have taken for handling this task from the background and threshold determination step to peak detection and integration step. We also demonstrate the effectiveness of this approach in handling measurments with dwell times that range from 50 ms to 10µs along with the examples of the data that were processed using this algorithm.

2:50pm - 3:00pm

FUN-OL 3: 4

Topics: Nanomaterials

Keywords: single particle ICP-MS, transport efficiency, calibration, protocols

A Study of the Particle Frequency and Particle Size Methods to Measure Transport Efficiency for the Counting and Sizing of Nanoparticles by Single Particle ICP-MS

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To date the most commonly used calibration scheme for the counting and sizing of nanoparticles (NPs) by spICP-MS, as outlined in Pace et al. [1], involves quantitation of the solution transport efficiency and measurement of the instrument response with ionic solution standards. Two methods for the measurement of the transport efficiency were presented, both of which conveniently require the use of only a single NP standard of known particle size and mass fraction; 1) the particle frequency method (PF-TE) which measures transport efficiency as the ratio of the number of particles entering the plasma to the number of particles introduced into the instrument and 2) the particle size method (PS-TE) which measures transport efficiency as the ratio of the mass of analyte measured in an ionic standard to the mass of analyte measured for the NP standard [1]. Good agreement between the PF-TE method and the PS- TE method was observed by Pace et al. and in the spICP-MS community, the PF-TE method is almost exclusively used to measure the transport efficiency as it is the simpler of the two methods to implement. However, in our laboratory when comparing transport efficiencies measured by both methods, we have observed statistically significant differences that impact the accuracy of the spICP-MS counting and sizing results.

In this talk we discuss possible causes for observed differences in the measured transport efficiency via the PF and PS methods. We investigate the influence of suspension stability, sample preparation protocols, and sample matrix on the transport efficiency measured by both methods, as well as evaluate results obtained using different instrument platforms. Transport efficiencies measured using NIST RM 8013 Gold Nanoparticles (Nominal 60 nm Diameter) and NIST RM 8017 PVP Coated Silver Nanoparticles (Nominal 75 nm Diameter) are compared and used to inform the expected accuracy of this calibration scheme. Our results show that exclusive use of the PF-TE method is not advisable.

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3:00pm - 3:10pm

FUN-OL 3: 5

Topics: Sample introduction and sample preparation, Glow discharge mass spectormetry, Coupling techniques (chromatography, FFF, ETV, others), Plasma source fundamentals, instrumentation and mechanisms

Keywords: ESI, DB-ESI, Ion-Focussing, Efficiency-Manipulation, DBDI

Focusing ions for ion trap based mass spectrometers - methods and applications

Sebastian Brandt, Alexander Schütz, Felix David Klute, Joachim Franzke

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The electrospray ionization method used for mass spectrometry (ESI-MS) is a well-established method for a broad spectrum of analytical approaches as proteomics, metabolomics, and genomics. It combines the possibility of ion creation of large macromolecules under atmospheric conditions without any noteworthy fragmentation or formation of adducts (soft ionization). Furthermore combining the ESI with separation techniques as high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), and free flow electrophoresis (FFE) delivers multitude of applications.

In general the electrospray (ES) process is based on electrostatic dispersion of liquids and thus produce aerosols. Therefore charged droplets are generated at the tip of a liquid/sample containing emitter influenced by a high electrical field. Highest at the tip the multi-charged droplets are accelerated by the electric field towards the MS continuously loosing solvent by evaporation and exploding by coulomb repulsion. The state of single or multiple charged ions abreast reaching the MS can be explained by the ion evaporation model (IEM) or charge residue model (CMR).

Based on the spray generation the used electrical field is high inhomogeneous comparable with discharges like atmospheric pressure chemical ionization (APCI). In combination with the coulomb repulsion of charged droplets such as ions it is conceivable that only the minority of ions will reach the inside of the mass spectrometer finally. There are several possibilities to enhance the ratio between produced and detected ions - called ion efficiency.

This presentation will concentrate on the electrical focusing based on an electrical lens system. It will be shown how to electrically variate the ion efficiency for commercial available nano-electrosprays (nESI) depending on the mass to charge ratio of the expected ions.

In case of the dielectric barriered form of an electrospray (DB-ESI) the static behavior of commercial available electrosprays will aggravate to a pulsed behavior of ion generation. The pulsed ion injection of ion trap based mass spectrometers makes the situation even more complicated. Therefore the requirements on the generator of the electrical pulse sequences increases dramatically. Although this characteristic - in case it is well understood - can enlarge the possibilities of DB-ESI. Also this deliver the spatio-temporal control of ions or multi-charged droplets with uncharged analytes of interests for possible coupling with plasma based ionization techniques like dielectric barrier discharge ionization (DBDI).

3:10pm - 3:20pm

FUN-OL 3: 6

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: DBDI, LTP, VUV, OES

Excitation and ionisation mechanisms in a complete dielectric barrier discharge (DBDI) and a partial dielectric barrier discharge (LTP)

Felix David Klute[1], Pascal Vogel[1], Sebastian Brandt[1], Charlotte Reininger[2], Daniel Thurston[2], Paul B. Farnsworth[2], Joachim Franzke[1]

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A dielectric barrier discharge is by definition given when a dielectric barrier is placed between the electrodes and at least one electrode is not in direct contact with the excited gas which forms the plasma [1]. This definition needs to be further refined to account for the differences that occur when either only one electrode or both electrodes of a discharge are covered by a dielectric barrier. It will be shown that additional excitation mechanisms emerge when a conducting material is introduced into the plasma volume as a grounded area. Quartz capillaries with a 1 mm inner diameter held in special 3D printed supports were used to ensure that potential observations can be solely attributed to either the presence or absence of a second dielectric barrier shielding the grounded electrode. Two representative geometries were chosen to conduct a systematic comparison namely the dielectric barrier discharge for ionisation (DBDI) representing the complete and the low temperature plasma probe (LTP) the partial DBD. While the DBDI is operated with two ring shaped electrodes that are placed outside of the capillary, only the powered electrode of the LTP is placed outside the capillary and the grounded wire electrode is placed inside the capillary and therefore in direct contact with the plasma. Measurements show that the LTP seems to create more charged species than the DBDI for comparable discharge parameters. Time and space resolved OES shows that an additional excitation mechanism occurs when a conducting surface is inside of the plasma volume. This superimposes the mechanisms that are already present when the grounded electrode would be outside of the capillary: it seems to be driven by secondary electron emission of the conducting surface yielding an additional source of electrons for the plasma. These secondary electrons are most likely produced by photons that are created right in the beginning of the early plasma period when already strong UV/VUV radiation from several highly excited species such as He^*/He^m, He_2^*,N_2^* or OH^* is present.

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3:20pm - 3:30pm

FUN-OL 3: 7

Topics: Environmental sciences

Keywords: HFSE; Ti; Zr; ICP-OES; Digestion

Determination of High Field Strength Elements (HFSE) in Soil & Mineral Samples by ICP Spectrometry after Microwave-Assisted High-Pressure Acid Digestion

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Hf, Zr, Ti, Nb and Ta are termed high field strength elements (HFSE) in geochemistry. Moreover, the determination of the Ti/Zr ratio in soils is very important for the reliable study of the uniformity of parent geological material between soil horizons which is the basis for evaluating any change of soil properties during pedogenesis or caused by soil mangagement. Additionally, the identification of lithologic discontinuities or differences in parent materials is a prerequisite for distinguishing soil properties of pedological origin from those of geological origin. When uniformity of parent material of a profile is established, changes in chemical, physical and mineralogical properties of soils along profiles can be attributed to pedogenic processes, and quantitative pedological studies on soils may be conducted. Comparing the ratios of the concentration of two resistant minerals between horizons is the most common method of assessing the uniformity of parent material. If elements are present exclusively in certain resistant minerals, such as Ti in rutile and Zr in zircon, the ratios of the elemental concentrations can also be used for identifying lithological breaks.

For the exact determination of HFSE in a sample, including the Ti/Zr ratio, the elements have to be recovered quantitatively from the soil matrix. Sample digestion can be carried out by fusion with either $Na_2B_4O_7$, Na_2CO_3 or $(NH_4)_2SO_4$. However, large amounts of reagents are needed and the system is prone to contamination. Additionally, due to the high salt content of the fusion solution, determination of the HFSE by ICP spectrometry is severely hampered. X-ray fluorescence, which can be used alternatively, suffers from matrix interferences and a lower sensitivity compared to ICP spectrometry.

The present method, based on high-pressure microwave-assisted digestion and element-specific detection by ICP-OES, will allow the determination of HFSE in soil samples, with special emphasis on Ti and Zr down to 0.5 mg/kg for each element.

MET-PL: METROLOGY - PLENARY LECTURE

Time: Monday, 20/Feb/2017: 4:10pm - 4:40pm
Location: ARLBERG-well.com NORTH HALL
Session Chair: Zoltan Mester
Session Chair: Anika Retzmann

4:10pm - 4:40pm

MET-PL: 1

Topics: Metrology in chemistry
Keywords: Metrology, Measurement Uncertainty, Comparability, SI, CRMs

Metrological principles in plasma spectrochemistry

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Metrological principles in plasma spectrochemistry

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ABSTRACT: Metrology, Science of measurement and its application, plays a vital role in today's world. It underpins almost every aspect of our everyday lives, such as industry and trade, quality of life, science and innovation. Metrology includes all theoretical and practical aspects of measurement, whatever the measurement uncertainty and field of application[1]. Metrology in chemistry has improved significantly in the last two decades as a result of efforts to achieve measurement comparability among countries. Comparability is achieved on a global scale when results are traceable to the same long-term stable measurement standards [ideally, the International System (SI) of Units] and continuously validated by regular inter-comparison exercises involving National Metrology Institutes (NMIs) through the auspices of the CCQM (Consultative Committee for Amount of Substance – Metrology in Chemistry) of the International Bureau of Weights and Measures (BIPM). NMIs disseminate traceability through calibration standards and matrix Certified References Materials (CRMs). Characterization of these materials demands utilization of the most accurate, precise and traceable measurement methodologies available. Inductively couple plasma mass spectrometry (ICP-MS) is one of the most popular plasma spectrochemistry based techniques, which has been extensively used to achieve traceable measurement results for trace elements, elemental speciation and isotopic ratios analyses. This lecture will highlight metrological principles and practices adapted at National Research Council Canada to achieve traceable and comparable measurement results using the common plasma spectrochemistry based technique ICP-MS or MC-ICPMS.

REFERENCES

1. JCGM200:2012, International vocabulary of metrology-Basic and general concepts and associated terms (VM), 3rd edition, 2012.

MET-IL: METROLOGY - INVITED LECTURES

Time: Monday, 20/Feb/2017: 4:40pm - 6:00pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Zoltan Mester

Session Chair: Anika Retzmann

4:40pm - 5:00pm

MET-IL: 1

Topics: Metrology in chemistry

Keywords: Chromium speciation, reference materials, reference methods

Speciation strategies for chromium in high carbon matrices using hyphenated QQQ-ICP-MS: Towards the production of new 'speciated' reference materials

Heidi Goenaga-Infante, Susana Nunez, Panayot Petrov, John Entwisle

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There is evidence to suggest that the different forms of Cr perform very different functions. Trivalent Cr (CrIII) may improve glucose and fat metabolism whereas hexavalent Cr (CrVI) is carcinogenic. More recently, concerns about the safety of dietary Cr (III) have been reported since this species were found to cause DNA damage in vivo[1].

Although several papers have reported methodology for the speciation of inorganic Cr species in a range of matrices, there are still remaining challenges[2] that may affect the achievement of comparability of results, in particular for samples with low µg kg^{-1} Cr levels and high carbon content.

One major challenge associated with the accurate quantification of inorganic Cr species is that the oxidation state of Cr can readily change, depending on pH and electrochemical potential of the exposing environment. In order to achieve maximised extraction efficiency of Cr(III) and Cr(VI) species from solids, previous studies have used alkaline hydrolysis but such methodology has only produced reliable data when used in combination with isotope dilution mass spectrometry calibration in order to minimise the effect of species redox inter-conversion on the accuracy of the speciation data. Moreover, the relatively high Cr blanks combined with the need for reducing spectroscopic interferences of $^{40}Ar^{12}C^{+}$ and $^{35}Cl^{16}O^{1}H$ on *m/z* 52 (e.g. by using increased instrument resolution, chromatographic selectivity or collision gases) make the accurate determination of inorganic species, with a fit-for-purpose measurement uncertainty, by HPLC-ICP-MS a difficult task. For these reasons, the development of reference methods and "speciated" reference materials is urgently needed to help establish quality control of existing methodology and for future risk assessments and regulation.

This lecture will describe development and validation of novel speciation strategies that overcome the challenges mentioned above through the use of "Cr-free" HPLC systems hyphenated to QQQ-ICP-MS in ammonia gas mode and ESI MS/MS. Examples of their application to (1) the speciation of Cr in tobacco smoke condensates and (2) the production of an organically-bound Cr-yeast reference material will be discussed. Focus will be on role of isotope dilution quantification in the provision of reference values for the characterisation of reference materials and for validation of more routine speciation measurements.

(1) European Food Safety Authority Journal, 2009, 1112, 1-20

(2) J. Scancar and R. Milacic, J. Anal. At. Spectrom., 2014, 29, 427-43

5:00pm - 5:20pm

MET-IL: 2

Topics: Metrology in chemistry

Keywords: double spike, mass fractionation, isotope abundance, molybdenum, strontium

Double-Spiking your way to successful isotope abundance measurements

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Subtle variations in the isotopic composition of many elements are providing unprecedented insights into the sources, processes and sinks of atoms in geological, biological, and cosmological systems. The challenge, however, is to ensure that the measured isotope abundances accurately characterize the isotopic composition of the analyte because mass dependent fractionation effects during sample preparation and subsequent measurement by mass spectrometry can exceed the natural fractionation processes under investigation. Fortunately, there are a number of strategies that may be employed to monitor and correct for analytical bias. Double-spiking is the ultimate approach that can deliver precise and accurate data provided some steps are taken in the design and implementation of the method. For example, thoughtful selection of the spike isotopes, the relative amount of spike added to the sample, and the method for correcting the measured data can significantly influence the results. It turns out that the application of a double-spike is not unspeakably complicated and there are many tools to assist in the design, execution, and data reduction of a spiked measurement. In this talk, I will describe how the double-spike method can be applied to isotopic systems that exhibit mass dependent (*e.g.* Mo) as well as non-mass dependent variations (*e.g.* Sr) in isotopic composition. Methods for calculating the isotopic composition of the sample will be presented along with suggested resources to help users have the double-spike running successfully in their laboratories. Examples of applications of Mo and Sr isotope abundance data to study sources and mixing of ground and surface waters will be shown.

5:20pm - 5:40pm

MET-IL: 3

Topics: Metrology in chemistry

Keywords: measurement uncertainty; Monte Carlo Simulations; Microsoft Excel

Who is afraid of Monte Carlo Simulations? An easy way to estimate combined measurement uncertainty using standard spreadsheet software

Thomas Walczyk

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The nature of chemical measurements implies that a measurement result is incomplete without a probability statement, commonly expressed as a standard deviation. However, measurement repeatability and reproducibility contribute but are rarely equal to the estimated 'combined measurement uncertainty' – which considers all identifiable sources of random and systematic error in the measurement result.

While this basic metrological concept is now broadly recognized, it is still not widely implemented in laboratory practice. Establishing a measurement model that connects input variables and the measurement result in the form of an equation is not a difficult task. It is necessary for calculating the result anyhow. But combining uncertainties in all input variables into a single combined uncertainty estimate of the measurement result (which can exceed measurement repeatability multiple times) is a hurdle that not many chemists are willing to take. Set-up of complex differential equations and their solution seems to be overly complicated and too time consuming.

This talk is meant to change this perception and is intended to demonstrate to the practical analytical chemist that error/uncertainty propagation analysis can be accomplished within 5-15 min even for highly complex analytical methods with minimal knowledge in algebra. This becomes possible by using standard spreadsheet software (Microsoft Excel) for numeric modelling of repeated analytical runs, a process widely known as 'Monte Carlo Simulation' [1]. The latter is recognized by the International Bureau of Weight and Measures (BIPM) in Supplement 1 of its authoritative 'Guide to the Expression of Uncertainty in Measurement (GUM)' as a valid approach for estimating measurement uncertainty [2].

Monte Carlo Simulations can be also most helpful for the optimization of a measurement strategy and to make an analytical method 'fit for purpose'. In many applications, representative sampling is a major challenge and sampling uncertainty can be much larger than analytical uncertainty. In such a case, efforts to improve measurement accuracy and repeatability may turn out to be redundant. Instead, reduction of analytical costs and analysis time for increasing sample throughput might be the better strategy. This will be illustrated using a real-world example aiming at authentication of chicken eggs for geographical origin and production technique using stable isotope signatures.

[1] Chew G. and Walczyk T. (2012) A Monte Carlo approach for estimating measurement uncertainty using standard spreadsheet software. Anal. Chem. 402:2463–2469.

[2] BIPM (2008) Guide to the expression of uncertainty in measurement - Supplement 1: Propagation of distributions using a Monte Carlo method; Joint Committee for Guides in Metrology (JCGM)

5:40pm - 6:00pm

MET-IL: 4

Topics: Isotope ratio analysis, Metrology in chemistry

Keywords: IDMS, uncertainty of measurement, reference materials, CITAC, award

Plasma Spectrometry Contributions to Metrology in Chemistry*

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As reliability and accuracy of results from plasma spectrometry have improved over the decades methods based on these techniques have yielded a number of useful procedures for metrology in chemistry applications. Additionally, the supreme detection power as well versatile sample preparation and sample introduction principles have widely increased the applicability of plasma spectrometry.

Particularly the versions of plasma spectrometry based on mass detection have greatly helped to produce results that are traceable to the SI-unit mole. A major move in this direction is spurred by the introduction of ID (isotope dilution) procedures where the connection to SI is so close – and consequently the realization of traceability is so superb – due to the low uncertainties of measurement that are achievable by this technique.

It will be demonstrated that the small combined uncertainty is mainly caused by cancellation of otherwise dominating contributions to uncertainty, while the only new ones are the ability to produce the isotopic spike in a chemically equivalent form to that in the sample and the perfect homogenization of this spike in the sample. Where this can be achieved the resulting procedure is almost uniformly superior to any other technique, thereby providing an excellent tool for the certification of reference materials that subsequently can be distributed through NMIs (National Metrology Institutes) or other suppliers.

CITAC – The Cooperation on International Traceability in Analytical Chemistry, www.citac.cc – has been sponsoring for some time a yearly metrology award for the best paper published. Mass spectrometry methods have been employed frequently by the winners of this award. As few examples will serve to demonstrate the power of plasma spectrometry in this context.

*dedicated to the memory of the late Paul de Bièvre

MET-OL: METROLOGY - GENERAL SESSION

Time: Monday, 20/Feb/2017: 6:00pm - 7:10pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Zoltan Mester

Session Chair: Anika Retzmann

6:00pm - 6:10pm

MET-OL: 1

Topics: Metrology in chemistry

Keywords: Proficiency Tests, Trace Elements, Reproducibility

Comparison of performances between ICP-OES and ICP-MS in trace elements analysis on water and soils: the Italian experience of UNICHIM Proficiency Tests

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UNICHIM, the Italian Association for Standardization in Chemistry, since more than 15 years has developed and organized Proficiency Tests on environmental matrices (water and soil) with a very wide participation of the Italian Laboratories (more than 400 laboratories are consistently participating to these PT schemes).

This huge amount of data (more than 90,000 results for trace elements) constitutes a significant overview of the analytical performances both for different analytical techniques and analytes.

In this presentation the results of the last 5 years of activity are presented, showing the best performances reached by using ICP-MS and ICP-OES techniques in the determination of As Be Cd Co Cr Cu Hg Mn Ni Sb Se Sn V Tl Zn in environmental samples.

A comparison between the two techniques is presented, showing where comparable results between ICP-OES and ICP-MS methods can be expected and when significant interference or sensitivity problems can arise.

The accuracy and reproducibility standard deviation obtained in these PT schemes are presented.

6:10pm - 6:20pm

MET-OL: 2

Topics: Sample introduction and sample preparation, Elemental analysis, Environmental sciences
Keywords: Seawater, ICP-QQQ-MS, Column Chelation, Hydride, Rare Earth Elements

Reducing the risk of inaccurate results when quantifying trace elements in seawaters using ICP-QQQ-MS

Tamas M Ugrai, Hakan Gürleyük, Geoff Leadbeater, Michelle Briscoe
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Determination of low-level trace metals and rare earth elements in seawaters by ICP-MS is usually complicated by significant matrix effects and polyatomic interferences. To overcome these issues, multiple off-line and on-line techniques can be employed. However, certain methods to reduce or overcome the complex matrix will be more appropriate depending on the analyte of interest, oxidation state of the analyte, and specific matrix parameters. This paper presents lessons learned from multiple years of analyzing thousands of seawater samples, supported by data that shows potential biases that can arise when incorrect methods are employed. On-line column chelation is a commercially available preconcentration system where a variety of trace elements are first acid solubilized, then neutralized with a buffer solution to allow chelation onto a iminodiacetate functionalized resin. Large volumes of an aqueous sample can be used to preconcentrate solubilized metals onto the resin. Group I and II metals, as well as many anions, are selectively removed from the resin by washing with an ammonium acetate buffer, significantly reducing matrix interferences. The metals of interest are then washed off the resin by elution with a small aliquot of dilute nitric acid and quantified by ICP-MS. Unfortunately, this method is not applicable for metalloids such as As and Se that exist as anions. In addition, certain matrix components, such as dissolved organic carbon (e.g., humic acid) and complexing agents may interfere with the chelation process and cause biased data. Detection limits for transition metals have been established in the 0.2 – 5 ng/L range, while ultra-low detection limits for some rare earth elements are in the 0.5 - 5 pg/L range when this technique is coupled to an ICP-QQQ-MS instrument. Another technique routinely used is on-line hydride formation where sodium borohydride is added to the sample creating hydrides of elements such as As, Se, and Sb. The hydrides leave the seawater matrix behind and are transferred to the ICP-QQQ-MS. While hydride generation coupled to a sophisticated instrument such as an ICP-QQQ-MS can provide extremely low detection limits, it is still prone to the species-specific challenges. For instance, it is very well known that Se(VI) does not form a hydride, and unless it is converted to hydride active Se(IV) prior to analysis, producing biased data is unavoidable. While technology and analysis automation move forward at a fast pace, it is still important to focus on the chemistries involved with the analysis of seawaters to avoid significant biases in the data. Results from the analysis of real world samples and corresponding quality control data will be presented on the accuracy, specificity, and reproducibility of the methods listed above, highlighting potentially disastrous issues that can be encountered in a fast-paced laboratory environment. For each challenge, this paper presents solutions for overcoming the issues.

6:20pm - 6:30pm

MET-OL: 3

Topics: Elemental analysis, Isotope ratio analysis, Application of speciation analysis, Metrology in chemistry

Keywords: Certified reference materials, Apple juice, Arsenic speciation, Isotope dilution mass spectrometry, Standard Addition

Development of an apple juice certified reference material for cadmium, lead, total arsenic and arsenic species

Fransiska Dewi, Lay Peng Sim, Juan Wang, Benny Meng Kiat Tong, Richard Y.C Shin, Tong Kooi Lee

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Heavy metals are common contaminants in food. Several major organisations such as World Health Organisation (WHO), US's Food and Drug Administration (FDA) and Europe's Environmental Protection Agency (EPA) have issued advisories and regulations on the limits of heavy metals in food and water, including beverages. To ensure that the samples being tested comply with regulatory limits, it is essential that testing laboratories have reliable and validated methods to determine the level of heavy metals present. Certified reference materials (CRMs) are important for these testing laboratories in the validation of their methods. They are also ideal candidates for use as quality control materials.

Recently, our laboratory developed an apple juice CRM containing cadmium, lead, inorganic arsenic [As(III) and As(V)], as well as organoarsenic (DMAA) species. The development of the CRM, which included procedures for sample preparation, homogeneity study, stability study, assignment of reference values and uncertainty evaluation, was carried out in accordance with the requirements of ISO Guides 34:2009 and 35:2006 [1,2].

Isotope dilution mass spectrometry (IDMS) method was used for the assignment of reference values and long-term stability study for cadmium and lead. For total arsenic, inorganic arsenic, as well as dimethylarsenic acid, standard addition method was used. The measurements were carried out using inductively coupled plasma mass spectrometer (ICP-MS), sector field ICP-MS or HPLC coupled with ICP-MS (for arsenic speciation). The analytes were found to be homogenous and stable over a period of at least 4.5 months at storage temperature of -20°C (long-term stability).

This presentation gives an overview of the development process of the CRM, as well as the approach taken by our laboratory to ensure that the certified values are traceable to the SI.

[1] ISO Guide 34:2009 General requirements for the competence of reference material producers

[2] ISO Guide 35:2006 Reference materials – General and statistical principles for certification

6:30pm - 6:40pm

MET-OL: 4

Topics: Sample introduction and sample preparation, Elemental analysis

Keywords: food chemistry; trace metals in milk; on-line isotope dilution; ICP-MS

MULTI-ELEMENTAL DETERMINATION OF TRACE METALS IN MILK BY ON-LINE ISOTOPE DILUTION AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY USING A HIGH EFFICIENCY SAMPLE INTRODUCTION SYSTEM

Rachida Chekri, Nathalie Marchond, Thierry Guérin, Petru Jitaru

Université Paris-Est, Anses, Laboratory for Food Safety, F-94700 Maisons-Alfort, France; petru.jitaru@anses.fr

The presence of traces of toxic metals in foodstuff is still a matter of concern at national and European level. Milk is one of the matrices of high interest in terms of contamination with trace metals due to its large consumption by the general population, particularly by children. Apart from the metals already regulated by EU in foodstuff (Pb, Cd and Hg), other metals, such Cr, Ni, etc. have become of interest in the last years due to their potential toxicity. Milk is a peculiar matrix to analyze because of the presence of large quantities of proteins, lipids, sugars and minerals in its composition. The conventional methods for trace metals determination in milk rely on acidic microwave digestion and measurement by inductively coupled plasma mass spectrometry (ICP-MS). This approach is rather laborious and environmentally non-friendly because of the use of concentrated acids.

This works aims at the development and validation of a method for the determination of several trace metals (Pb, Cd, Hg, Cr, Ni,…) in various types of milk by using on-line isotope dilution and inductively coupled plasma mass spectrometry (ON-ID-ICP-MS). For this purpose, the trace metals were determined in the milk whey that was obtained by centrifugation of various types of milk (whole, semi-skimmed and skimmed milk). The milk whey was purified by using an ultra-centrifugal membrane (10 kDA). The samples were discretely introduced into the ICP-MS by using a liquid chromatography (LC) system (without column) equipped with an autosampler. The multi-elemental spike solution was mixed with the sample contained in the LC carrier by an additional peristaltic pump and a T-connection. Various samples carriers (and their flow rate) such as pure water and diluted solutions of HNO_3 and methanol (1-3%) were tested in order to achieve maximum signal stability. The matrix effects and the sensitivity were modulated by varying the volume of the sample introduced discretely into the ICP-MS *via* the LC injection system. A high efficiency sample introduction system (APEX™ Q) was also used for sensitivity enhancement (up to 10 fold, depending on the analyte). ON-ID-ICP-MS combined with discrete sample introduction allows full automatization of the analytical procedure without sample digestion and without the use of an external calibration hence increasing the overall simplicity and sample throughput. The accuracy was evaluated by comparison with an accredited method (external calibration) for multi-trace metals determination in food matrices.

6:40pm - 6:50pm

MET-OL: 5

Topics: Elemental analysis, Isotope ratio analysis, Metrology in chemistry
Keywords: ICP-MS, ICP-OES, ID-ICP-MS, trace metals, drinking water

Application of isotope dilution, standard additions calibration strategies in ICP-MS analysis and external calibration strategy in high resolution ICP-OES analysis of Sr, Pb, Na, Cu in drinking water

Vladimir Ivanovich Dobrovolskiy, Aleksei Anatolievich Stakheev, Dmitriy Dmitrievich Frolov
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The determination of trace metals in drinking water is an important measurement responsibility. There is no single approach that is universally applicable, as the nature and regulations for drinking water standards may vary among countries and regions. Target concentrations were chosen to approach the maximum acceptable The World Heath Organization's limits. The relatively high mass fraction of sodium simulates the matrix of natural fresh water. The present paper describes the contribution of the Russian Metrological Institute of Technical Physics And Radio Engineering to the measurement of Na, Sr, Cu and Pb amount contents in a drinking water sample, in SIM.QM-S7 «Supplementary Comparison for Trace Metals in Drinking Water». The analytical procedure to establish the values Sr and Pb amount contents was based on isotope dilution inductively coupled plasma-mass spectrometry (PlasmaQuant MS, Analytik Jena) and the values Na and Cu amount contents was based on standard additions inductively coupled plasma-mass spectrometry (PlasmaQuant MS, Analytik Jena) as well as all 4 elements was measured on external calibration high resolution inductively coupled plasma – optical emission spectroscopy (PlasmaQuant PQ 9000 Elite, Analytik Jena). Applying those procedures values, traceable to the SI, were obtained for the drinking water, which was collected in Ottawa, filtered and acidified to pH 1.6 to provide stability. For each of the amount contents presented here a total uncertainty budget was calculated using the method of propagation of uncertainties according to ISO and EURACHEM guidelines. The measurement procedures, as well as the uncertainty calculations are described. In order to keep the whole certification process transparent and so traceable, the preparations of various reagents and materials as well as the sample treatment and blending, the measurements themselves, and finally the data treatment are described. As the confirmation of the applicability of these procedures the results of comparisons SIM.QM-S7 (15 national metrological institutes of the different countries participated) are shown.

6:50pm - 7:00pm

MET-OL: 6

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metrology in chemistry
Keywords: Dental implants, LA-ICP-MS, Soft tissues, Calibration strategies, Bioimaging

LA-ICP-MS as a tool for mapping of Ti, Al and V released from dental implants to soft tissues

Adam Sajnóg[1], Anetta Hanć[1], Krzysztof Makuch[2], Ryszard Koczorowski[2], Danuta Barałkiewicz[1]
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Dental implants are used to replace missing teeth, including complete edentulism. The most commonly used metal in the implantology is titanium, which is characterized by high resistance to mechanical wear and corrosion, and is generally well tolerated by the human body. Implant contact with body fluids can cause galvanic corrosion, as a result of which the metal ions, which are components of the implant, penetrate into the surrounding tissue. There is a risk of lack of biocompatibility and allergic reactions leading to inflammation or even rejection of the implant.

The aim of the conducted research was to develop a method of quantitative analysis of elements (Ti, Al, V) in soft tissues by LA-ICP-MS and to examine fragments of oral mucosa tissues collected from patients treated with dental implants.

LA-ICP-MS was used for in situ quantitative analysis of the oral mucosa in patients before and after treatment with titanium implants. According to used implant system, the intraosseous part of an implant and the temporary closing screw is composed of ca. 99% Ti or Ti6Al4V alloy with composition ca. 90% Ti, 6% Al and 4% V. Measurements were made using a quadrupole ICP-MS (Elan DRC II, PerkinElmer) with a laser ablation system (LSX-500, Cetac). Two calibration strategies have been developed based on the solid standards with analyte addition with a matrix similar to the analyzed tissue. A novel approach was the use of powdered egg white as the matrix material due to the similar composition to that of the examined tissue. In the second approach a certified reference material (CRM) - Bovine Muscle ERM-BB184 was used as the matrix material. The isotope ^{34}S has proven to be the most suitable as the internal standard. Other isotopes (^{13}C, ^{26}Mg, ^{43}Ca) also were tested as potential internal standards. The calibration procedure has been checked for suitability for use in soft tissue analysis by determining validation parameters. The dynamic ablation of the whole oral mucosa surface was applied which allowed for the preparation of two-dimensional maps of content of the analytes. As a result of placement of the implant in the patient's body, analyte levels in the examined tissues were significantly higher than in control tissues. Analytes are unevenly distributed on the surface of tissues and show local, sharp maximal content.

This work was financially supported by the Research Project of the National Science Centre Poland (2015/17/N/ST4/03808).

Literature:

[1] A. Sajnóg, A. Hanć, K. Makuch, R. Koczorowski, D. Barałkiewicz, Spectrochim. Acta Part B 125 (2016) 1–10.
[2] A. Hanć, A. Piechalak, B. Tomaszewska, D. Barałkiewicz, Int. J Mass Spectrom. 363, (2014) 16–22.
[3] D.A. Frick, D. Gunther, J. Anal. At. Spectrom. 27 (2012) 1294–1303.
[4] J.S. Becker, M. Zoriy, A. Matusch, B. Wu, D. Salber, C. Palm, J.S. Becker, Mass Spectrom. Rev. 29 (2010) 156–175.

7:00pm - 7:10pm

MET-OL: 7

Topics: Metrology in chemistry

Keywords: HPLC/LA-ICP-MS; Isotope dilution; transferrin; albumin

Determination of transferrin, albumin and electrolytes in human serum CRM by using isotope dilution HPLC/Laser ablation-ICP-MS

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Transferrin (Tf), albumin (Alb) and Electrolytes are of vital importance for pathological state monitoring and clinical diagnosis. In this work, the electrolytes （K, Ca and Mg）in human serum were determined by using isotope dilution ICP-MS with a cold plasma and collision reaction cell mode. For the quantification of Tf and Alb in human serum, two strategies based on isotope dilution ICP-MS via sulfur/iron determination were used. In the post-column species-unspecific isotope dilution HPLC-ICP-MS approach, by introducing isotopically enriched ^{34}S and ^{54}Fe spikes at the same time, the human serum Tf and Alb were absolutely quantified via both sulfur and iron. In the other strategy, we report the absolute quantification of Tf and Alb in human serum by non-denaturing (native) GE combined with species-unspecific isotope dilution laser ablation-ICP-MS. In this method, to achieve a homogeneous distribution of both protein and isotope-enriched spike, immersing the protein strips after gel electrophoresis with ^{34}S spike solution was demonstrated to be an effective way of spike addition. Furthermore, effects of immersion time and ^{34}S spike concentration were investigated to obtain optimal conditions of the post-electrophoresis isotope dilution method. The human serum protein certified reference material (ERM-DA470k/IFCC) was used for method validation, and the results were in agreement with the certified value with good precision and small uncertainty (1.5~3%).

SPEC-PL: SPECIATION - PLENARY LECTURE (AGILENT PLASMA AWARD)

Time: Tuesday, 21/Feb/2017: 8:30am - 9:00am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Jörg Feldmann

Session Chair: Magdalena Dorothea Blanz

8:30am - 9:00am

SPEC-PL: 1

Topics: Application of speciation analysis

Keywords: speciation

Conferring a molecular dimension to ICP MS: chemical speciation analysis and -omics

Joanna Szpunar

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The outstanding features of ICPMS in terms of detection limits, multiisotopic capability and matrix tolerance have made it a technique of choice for trace and ultratrace metal analysis in biological systems. However, the use of a high energy plasma results in a loss of the information about the chemical environment (species) of the metal measured.

The growing awareness of the importance of the chemical speciation information [1] led to the use of ICP MS as a detector in HPLC [2]. In this way, the molecular selectivity could be assured by the differentiation of the species according to their physicochemical properties on-line prior to ICP MS.

The advent in mid90ties of electrospray MS indicated the potential of this technique as ultimate tool of speciation analysis. However, very strong matrix dependent effects were responsible for massive false negatives. A breakthrough towards the democratization of electrospray MS/MS for speciation analysis was the development of ICP-MS-controlled multidimensional HPLC approaches [3,4]. In this way, the mass balance of the metal eluted from the column could be precisely controlled, the sequential use of different separation mechanisms lead to the chemically pure peaks enabling metal species cartography and, in most cases, their electrospray MSn analysis. Integrated HPLC-ICP/ESI MS systems using this concept were ultimately proposed [5].

The concept of the ICP-MS-controlled species purification for ESI MS was later proposed to be integrated in canonical metalloproteomics and metabolomics protocols allowing the extraction of metal-related information on the entire proteome or metabolome scales (metallomics) [6]. Subsequent advances in couplings of different separation mechanisms (e.g. HILIC) and formats (e.g. nanoHPLC) to ICP MS have followed. In parallel, the progress in ESI FT MS, offering high resolution and accuracy of mass measurement and intrascan dynamic range has made structure elucidation quasi-routine.

The lecture discusses the current, still unchallenged, position of ICP MS in speciation analysis and metallomics illustrated by a number of examples relevant to the environmental, food and clinical analysis drawn from research in the author's laboratory. It also analyses the potential of ESI FT MS as a self-standing tool in speciation analysis in foreseeable future.

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[2] Dean, J.R., Munro, S., Ebdon, L., Crews, H.M., Massey, R.C (1987) JAAS., 2 , 607

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[4] Szpunar, J., Łobiński, R. (2002) Anal. Bioanal. Chem., 373, 404

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[6] Mounicou, S., Szpunar, J., Lobinski, R. (2009) Chem.l Soc. Rev., 38, 1119

SPEC-IL 1: SPECIATION - INVITED LECTURE 1

Time: Tuesday, 21/Feb/2017: 9:00am - 9:20am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Jörg Feldmann

Session Chair: Magdalena Dorothea Blanz

9:00am - 9:20am

SPEC-IL 1: 1

Topics: Elemental analysis, Application of speciation analysis

Keywords: Arsenic, Speciation analysis, HPLC-ICPMS

The Importance of Plasma Spectrochemistry for Arsenic Speciation Analysis

Walter Goessler

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Before the introduction of ICPMS about 30 years ago, atomic absorption spectrometry was the method of choice for arsenic analysis. Hydride generation was often employed as sample introduction to improve the otherwise poor detection limits. A major drawback of hydride generation was the uneven response for the different arsenicals depending on the analytical conditions. Arsonio compounds were not even accessible without an alkaline digestion. ICPMS in contrast gave almost the same response for all the arsenic compounds known at that time. Therefore, ICPMS has become an indispensable tool for arsenic determination in various matrices. Life science, medicinal and environmental applications are, besides nuclear industry and semiconductor industry, major fields of application. Due to the new USP regulations ICPMS is of increasing importance in the pharmaceutical area.

In 1988 Canadian researchers coupled for the first time liquid chromatography to ICPMS for the determination of the arsenic compounds in a certified reference material [1]. In the following years ICPMS was frequently used as an element-selective detector for arsenic speciation analysis of marine samples. Until 1995 it was common knowledge that more complicate arsenic compounds are only occurring in the marine environment, whereas in the terrestrial environment only inorganic arsenic, dimethylarsinic acid and methylarsonic acid are present. With the help of ICPMS as element-selective detector arsenobetaine was for the first time detected in mushroom samples [2]. From this moment on all arsenic compounds previously only attributed to the marine environment were also found in terrestrial samples albeit at much lower concentrations. With the implementation of the collision/reaction cell technology traces of arsenic compounds were detectable even in really difficult matrices. In 2004 thiolated arsenicals have been discovered as naturally occurring arsenicals [3]. Research on lipid-soluble arsenic – today an emerging field in arsenic speciation analysis – has also been initiated with the help of ICPMS in 2008 with the discovery of arsenic-containing fatty acids in fishoil samples [4].

Due to the permanent improvement of the instrumentation ICPMS has now become a routine detector for arsenic speciation analysis in various fields. In 2009 the EFSA concluded that HPLC-ICPMS has become the method of choice for arsenic speciation analysis in food. 2016 a European Norm (EN 16802) for the determination of inorganic arsenic in foodstuffs of marine and plant origin by anion-exchange HPLC-ICPMS following waterbath extraction was published. In the presentation historical aspects as well as recent developments in arsenic speciation analysis are discussed.

[1] Beauchemin D. et al. Anal. Chem. 60, 2209-2212 (1988)

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[3] Hansen, H.R. et al. Chem. Res. Toxicol. 17, 1086-1091 (2004)

[4] Rumpler, A. et al. Angew. Chem. 47, 2665-2667 (2008)

SPEC-OL 1: SPECIATION - GENERAL SESSION 1

Time: Tuesday, 21/Feb/2017: 9:20am - 10:00am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Jörg Feldmann

Session Chair: Magdalena Dorothea Blanz

9:20am - 9:30am

SPEC-OL 1: 1

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis

Keywords: drug metabolism, total drug exposure, metabolite profiling, inductively coupled plasma – tandem mass spectrometry

Determination of the total content of drug-related chlorine and chlorine speciation in human blood plasma using high performance liquid chromatography – tandem ICP-mass spectrometry (HPLC-ICP-MS/MS)

Balazs Klencsar[1], Eduardo Bolea-Fernandez[1], Maria R. Florez[1], Lieve Balcaen[1], Filip Cuyckens[3], Frederic Lynen[2], Frank Vanhaecke[1]

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In a first phase of this work, a fast, accurate and precise method for the separation and determination of the total contents of drug-related Cl and Br in human blood plasma, based on high performance liquid chromatography - inductively coupled plasma - tandem mass spectrometry (HPLC-ICP-MS/MS), has been developed[1]. The novel approach developed has been proved to be a suitable alternative to the presently used standard methodology (*i.e.* based on a radiolabelled version of the drug molecule and radiodetection), while eliminating the disadvantages of the latter. Interference-free determination of ^{35}Cl has been accomplished via ICP-MS/MS using H_2 as reaction gas and monitoring the $^{35}ClH_2^+$ reaction product ion at mass-to-charge ratio of 37. Br could be measured "on mass" at a mass-to-charge of 79. HPLC has been relied on for the separation of the drug-related entities from the substantial amount of inorganic Cl. The method developed has been found to be sufficiently precise (repeatability < 10% RSD) and accurate (recovery between 95 and 105%) and shows a linear dynamic range (R^2 > 0.990) from the limit of quantification (0.05 and 0.01 mg/L for Cl and Br in blood plasma, respectively) to at least 5 and 1 mg/L for Cl and Br, respectively. Quantification via either external or internal standard calibration provides reliable results for both elements. As a proof-of-concept, human blood plasma samples from a clinical study involving a newly developed Cl- and Br-containing active pharmaceutical ingredient have been analysed and the total drug exposure has been successfully described. Cross-validation has been achieved by comparing the results obtained on Cl- and on Br-basis.

This project is currently focusing on method development for quantitative metabolite profiling of Cl-containing drugs via a combination of reverse-phase (RP) HPLC for the separation of the drug metabolites from one another and ICP-MS/MS for Cl monitoring. The effect of gradient elution on ICP-MS sensitivity has been systematically investigated, taking the most important chromatographic parameters – e.g., organic solvent composition, type of organic modifier, slope of gradient, flow rate, eluent additives – into account. The main system suitability requirements (e.g., tailing factor, theoretical plate number, system precision) have been assessed taking into account the expectations of pharmaceutical authorities, and a comparison with the values attainable using HPLC-UV will be provided. The final goal is the demonstration of the utility of HPLC-ICP-MS/MS in the context of real-life applications.

[1] Balázs Klencsár, Eduardo Bolea-Fernandez, María R. Flórez, Lieve Balcaen, Filip Cuyckens, Frederic Lynen and Frank Vanhaecke; Determination of the total drug-related chlorine and bromine contents in human blood plasma using high performance liquid chromatography – tandem ICP-mass spectrometry (HPLC-ICP-MS/MS), *J. Pharm. Biomed. Anal.*, **124** (2016) 112-119.

9:30am - 9:40am

SPEC-OL 1: 2

Topics: Application of speciation analysis, Metallomics

Keywords: Selenium, selenosugar, isotope dilution, human cells, ICP-MS

Small selenium species in human liver cells: Investigations of their cytotoxicity, bioavailability and metabolism by means of isotope dilution (HPLC-) ICP-QQQ-MS methods

Talke Anu Marschall[1], Julia Bornhorst[1], Björn Meermann[2], Doris Kühnelt[3], Tanja Schwerdtle[1]

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The essential trace element selenium (Se) owns a narrow range between minimum and tolerable upper intake level (60 – 300 µg/d)[1,2], because it may induce toxic effects following elevated uptake. It is taken up *via* the diet in various forms. Among these, small species like selenomethionine (SeMet), methylselenocysteine (MeSeCys) and selenite play a central role. However, their metabolism and their toxic modes of action are not fully understood until today.

In this study, we aim at comparing cytotoxic effects, cellular uptake and metabolism of SeMet, MeSeCys and selenite as well as the two major human urinary metabolites, methyl-2-acetamido-2-deoxy-1-seleno-β-D-galactopyranoside (selenosugar **1**) and the trimethylselenonium ion (TMSe). As a cellular model system human liver cells were used for incubations with the respective Se species. To achieve sensitive Se detection in cellular matrices, ICP-QQQ-MS was deployed by detecting the most abundant Se isotopes ^{80}Se (49.61%) and ^{78}Se (23.78%). As these isotopes are strongly isobarically interfered, ICP-QQQ-MS was operated in on-mass and mass-shift mode with oxygen and hydrogen as reaction gases, which successfully eliminated interferences. For quantifying cellular total Se (ICP-QQQ-MS) as well as Se species (HPLC-ICP-QQQ-MS) species-unspecific on-line isotope dilution was applied with an isotopically enriched ^{77}Se spike.

As a result, distinct species-specific effects were observable by the aforementioned techniques: Inorganic selenite significantly reduced the cell number in low µM concentrations, while MeSeCys and SeMet induced effects in high µM concentrations. In contrast, the urinary metabolites were non-toxic up to supra-physiological concentrations despite significant total Se concentrations in the incubated cells. Speciation analysis revealed that both urinary metabolites were present in the cell lysates in an untransformed manner. SeMet and MeSeCys were partly metabolised to unknown Se species and selenite was predominantly incorporated by the cells. These results demonstrate that Se cytotoxicity in human cells strongly depends on the Se species and not necessarily on total cellular Se. Most likely, the extent of cellular biotransformation and species-specific modes of action are responsible for the species-specific cytotoxic effects.

[1] AP Kipp, D Strohm, R Brigelius-Flohé et al. Revised reference values for selenium intake. *Journal of Trace Elements in Medicine and Biology*. 2015;32

[2] European Commission, 2000. Opinion of the Scientific Committee on Food on the Tolerable Upper Intake Level of Selenium

9:40am - 9:50am

SPEC-OL 1: 3

Topics: Application of speciation analysis, Metallomics

Keywords: ICP-MS, Selenoprotein P, Isotope Dilution, Speciation, Se-peptides

Quantification of Selenoprotein P in serum using isotopically-enriched seleno-peptides and species-specific isotope dilution inductively coupled plasma mass spectrometry

Christian Deitrich[1], Susana Cuello-Nunez[1], Diana Kmiotek[1], Frank Torma[1], Maria-Estela Del Castillo Busto[2], Paola Fisicaro[2], Heidi Goenaga-Infante[1]

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Measurement results which are accurate, species-specific and comparable between laboratories are a requirement within the clinical community. Improving measurement results requires the development of traceable quantification methods for relevant species in biological fluids. A novel absolute quantification method for selenium (Se) bound to Selenoprotein P ($SEPP_1$), an important bio-marker for human nutrition and disease including diabetes and Alzheimer[1-2], is presented here for the first time. We report the use of a species-specific double isotope dilution mass spectrometry (SSIDA) in combination with HPLC-ICP-MS/MS approach for the determination of protein bound Se down to peptide level in a complex matrix at relevant concentration levels using small sample volumes. The method enabled the selective Se speciation analysis of human plasma samples without the need of extensive clean-up or pre-concentration steps as required for traditional protein mass spectrometric approaches. Critical considerations for using natural and isotopically enriched Se-peptides will be discussed. To assess the method accuracy, two plasma reference materials, namely BCR-637 and NIST SRM1950, for which literature data and a reference value for $SEPP_1$ have been reported, were analysed using complementary hyphenated methods and the species-specific approach developed in this work. The mass fraction of Se in $SEPP_1$ in the NIST material was determined as 60.6 µg kg^{-1} with a total combined relative measurement uncertainty of 5.35 % (k=2), which agrees well with the Se values reported by other national measurement institutes under the frame of the European Metrology Research Project EMRP HTL05 "Metrology for Metalloproteins".[3]The described method provides confirmatory values from the use of different isotope ratio pairs and different peptides used as calibrants and a full breakdown of the measurement uncertainty is provided. This is the first systematic approach for the quantification of a selenoprotein ($SEPP_1$) under relevant clinical conditions and it can be used for the certification of reference materials and the provision of reference values to clinical measurements and clinical trials.

(1) Rayman, **2012**. Lancet, **379**, 1256-1268

(2) Thomson, **1998**. Analyst, **123**, 827-831.

(3) Deitrich et al., **2016**. Anal. Chem., **88** (12), 6357–6365.

9:50am - 10:00am

SPEC-OL 1: 4

Topics: Application of speciation analysis, Environmental sciences

Keywords: Speciation, HPLC-ICP-MS, Arsenic, lichens, biomonitoring

Optimized arsenic speciation using anion exchange HPLC-ICP-MS for lichen air pollution biomonitoring

Eve Mariel Kroukamp[1], Patricia Belinda Crosby Forbes[1], Taddese Wondimu[2]

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The analysis of ultra-trace concentrations of arsenic in biomonitors of air pollution can be challenging, where matrix effects and spectral or mass spectrometric interferences can negatively impact analyses with inorganic mass spectrometry. A further challenge relates to establishing a mass balance between the total arsenic and the respective inorganic and organic chemical species extracted from the plant material, which is required if the toxicity, environmental cycling and fate of this carcinogenic metalloid is to be known. Speciation studies require that the sampling, sample preparation and mobile and stationary phases do not compromise species integrity, while simultaneously ensuring that the species of interest has sufficient resolution. The speciation of inorganic forms of arsenic in biomonitors of air pollution, such as lichens, is not widely researched, as numerous species of arsenic may be present and co-elution of species may pose a problem. One of the well-documented interferences is the co-elution of arsenite (As III) with arsenobetaine (AsB) in anion-exchange chromatography. AsB species are then typically quantified using separate cation-exchange chromatography, and the As III concentration is determined by difference. Since the inorganic species of arsenic are often of primary interest due to their high toxicity, it would be ideal to rather be able to separate AsB from As III on the anion- exchange column without the need for an additional column.

We report the optimization of analytical variables for the speciation of five arsenic species in standard solutions and lichen samples (*Parmotrema austrosinense* Hale) from two sampling sites using HPLC-ICP-MS. Factors such as different mobile phases and flow rates were assessed for achieving adequate separation of arsenic species AsB, As III, dimethylarsenic acid (DMA), monomethylarsonium acid (MMA) and arsenate (As V). Injection volumes of 1 ppb As III and As V were also varied to determine the volume which would generate a measurable signal, without resulting in the tailing of peaks. The possibility of co-elution of an interfering species (chloride ions) was also explored. The combined concentrations of the five arsenic species, which were completely separated, comprised 7.62 and 7.69 % of the total arsenic concentrations in the lichen samples from the impacted (1.471 ± 0.12 ppb) and background (0.62 ± 0.444 ppb) areas respectively, where the concentration of As species in the impacted sample decreased in the order DMA>AsB>MMA>As III>As V whilst that from the background sample was MMA>DMA>AsB>As III>As V.

VS-VENDOR SESSION: Vendor oral presentations

Time: Tuesday, 21/Feb/2017: 10:40am - 12:20pm

Location: ARLBERG-well.com NORTH HALL
Session Chair: Carsten Engelhard
Session Chair: Anna Reese

10:40am - 10:50am

VS-VENDOR SESSION: 1

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: interface design, fundamentals, ion extraction

Improved Interface for High Sensitivity ICP-MS - Having Ion Kinetic Energy and Matrix Suppression Control

Iouri Kalinitchenko, Peter Zdaril
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Sensitivity is an important factor for the trace element analysis, especially for the precision, speed, LOD, etc. The sensitivity advantage in some cases can be compromised by the matrix suppression when a classical grounded Compargue Interface is used.

The classical Compargue Interface operates with **grounded** Skimmer cone, 2/3 submerged into the 'zone of silence'. In a low matrix sample we detect typical initial plasma positive space charge of +1…+3V at the skimmer cone tip under a hot plasma condition. The space charge strongly depends on the plasma gas temperature T_i and the electron temperature T_e According to the model the electrons are escaping the 'zone of silence' due to the 'Ambipolar diffusion' mechanism. The density N_e drops faster than N_i as the plasma expands due to high electron (e^-) mobility (m_e) compared to the ion mobility (m_i). Matrix elements can increase plasma density significantly adding another +1…+2V to the initial plasma space charge.

In our opinion, the main reason for the matrix suppression is the significant additional uncontrolled space charge build up at the skimmer cone tip for a matrix containing samples compared to a clean sample. Obviously, it is not the same to propagate a more dense, higher charged (containing matrix sample) plasma compared to a low density clean sample plasma through grounded skimmer cone tip.

Thus it is logical applying a positive voltage to the Skimmer to compensate the space charge making the cone electrically 'invisible' to the plasma.

We have studied: matrix signal suppression, ion Kinetic Energy Control and ion beam formation.

Experimental device: ICPMS (Analytik Jena) with modified Compargue (voltage controlled skimmer) interface.

Main results:

1. Positive skimmer cone voltage reduces matrix suppression. Applying +3…+6V eliminates the matrix suppression completely.
2. The sensitivity increase x10-100 times is obtained in Collision Cell (iCRC) mode when applying +3…+6V to the Skimmer cone.
3. Applying +3…6V to the Skimmer cone increases total ion current extracted from the plasma by a factor of 2 to 3 with unchanged 1mm diameter ion beam spot, measured by multi-pin electrometer.

The interface modification details, theory and experimental results will be discussed.

10:50am - 11:00am

VS-VENDOR SESSION: 2

Topics: Nanomaterials

Keywords: nanoparticle, microsecond, desolvator, detection limit

Improvement of the limit of detection for SP-ICP-MS using a desolvator and pseudo resolution to remove interferences with the HR-ICP-MS AttoM.

Ariane Karine Donard, Phil Shaw

Nu Instruments, United Kingdom; ariane.donard@nu-ins.com

Engineered nanoparticles are nowadays being used in in a multitude of industrial product. The release in the environment and the questions raised about a potential harm for the human health require the development of methodologies to characterise those materials. SP-ICP-MS has been proven in the last years to be an interesting tool for particle counting, sizing and quantification. The HR-ICP-MS AttoM allow the acquisition of signal with a dwell time down to 10 µs, (with no settling time). The combination of its fast signal acquisition capacity, its high sensitivity and the possibility to remove interference by increasing the resolution make the AttoM a promising instruments for this technique. In this work, the capacity of this instrument was discussed regarding the limit of detection achievable with the use of a desolvator or a pseudo resolution to resolve interferences.

Thanks to its high transmission efficiency, the AttoM already reaches low limit of detection for SP-ICP-MS in classical nebulisation introduction mode (6 nm for Au, Ag, CeO). In this work, the use of a desolvator to improve those limits of detection was discussed (4 nm for Au, Ag, CeO). The distinction between the sample transport efficiency and the ion extraction efficiency was compared to understand the increase in sensitivity.

The resolution capacity of the AttoM was also used for the size measurement of Fe_2O_3 nanoparticles for which the isotopes measured are interfered. For the AttoM, the independent control of source and collector slits also allow pseudo resolution. With this combination the flat top peak is conserved and the sensitivity is preserved compared to full resolution. The limits of detection reached for this nanoparticles were discussed.

11:00am - 11:10am

VS-VENDOR SESSION: 3

Topics: Elemental analysis

Keywords: Extractables and Leachables

Profiling Extractable and Leachable elements in ophthalmic drug containers, in accordance with USP<232> by ICP-MS and ICP-OES

Paige Elana Solomon, Jenny Nelson

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Standards and regulations are established to ensure pharmaceutical products are tested to ensure they are safe and effective. As part of these testing requirements, USP <232> calls for controlled experiments to verify that storage materials and conditions do not alter the elemental composition or toxicity profile of a drug. The concern is two-fold: First, certain elements, for example heavy metals, can be toxic at even trace levels of exposure, and second, elements or compounds that are unanticipatedly released into the drug formulation from packaging material will enter the body and can have adverse reactions with other medicines or endogenous biological processes. One such example is that redox properties of metals like copper, zinc, and iron have been implicated in the formation of cataracts and plaques in the eye, which lead to loss of vision (Bush & Goldstein, 2001; Hori et al., 2009). Thus it is critical that ophthalmic drugs are free of even trace concentrations of these metals (Bush & Goldstein, 2001). In this study, we investigated the elemental content of the plastic material of ophthalmic eye drop bottles using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) for the analyses. Data processing and evaluation was performed using Mass Profiler Professional (MPP) and Microsoft Excel. Specifically, we simulated harsh transport and storage conditions via high temperature and sonication to determine whether or not elements present in the polymer container migrated into the drug solution (extractables). The samples were allowed to sit for 50 days to identify changes in the extractables profile with storage, as well as to test the solutions under normal but extended conditions (leachables). Solvent pH and polarity were varied to produce extractables and leachables profiles for a range of mimicked drug matrices packaged in the plastic material studied, as well as to consider the extraction and leaching effects of changes in drug pH, which could potentially occur due to formulation decomposition and reaction over time. The results demonstrated statistically distinct elemental profiles, including released metals, that depended on solvent pH and polarity, temperature, and duration of storage. The data specifically suggests a strong correlation between the level of extractables released and the extraction temperature, and greater polymer decomposition in acidic and basic solutions compared to the more neutral drug formulations. In addition, higher contamination levels were detected in measurements immediately following stressed conditions compared to the re-measurement after the samples were stored for 50 days.

11:10am - 11:20am

VS-VENDOR SESSION: 4

Topics: Sample introduction and sample preparation

Keywords: Single Cell - ICP-MS, Metal Content, Nanoparticles

Single Cell ICP-MS – Monitoring the uptake of ionic and nanoparticulate metals in individual cells

Chady Stephan, Hamid Badiei, Samad Bazargan

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The introduction and development of Single Particle ICP-MS (SP-ICP-MS) has opened a new area of research which allows the rapid detection and analysis of metal-based particles in a variety of matrices and applications. The key feature of SP-ICP-MS is that it allows discrete pulses to be detected and measured in a time-resolved manner using microsecond (µs) data acquisition rates. This type of data acquisition is opening possibilities in other application areas where it can be applied. In this work, we will introduce the concept of Single Cell ICP-MS (SC-ICP-MS), where individual cells are rapidly analyzed for metal content as they enter the plasma.

This talk will focus of the theory and hardware needed for single cell ICP-MS analysis and discuss preliminary data form exposing fresh water algae (*Cryptomonas ovata*) to both ionic and nanoparticulate focusing on: Uptake of ionic metal *vs.* time, Uptake of metal nanoparticles (NP) *vs.* time, Quantification of uptake as number of particles / cell (or biological entity), Correlation of nanoparticle concentration with cell uptake rate, Insight into algae uptake during life cycle.

11:20am - 11:30am

VS-VENDOR SESSION: 5

Topics: Elemental analysis, Plasma source fundamentals, instrumentation and mechanisms

Keywords: ICP-MS, Instrumentation, Ease of Use, Interferences, Limits of Detection

The Combination of Superior Interference Suppression and Ease of Use – Recent Developments for Trace Elemental Analysis

Christoph Wehe, Shona McSheehy Ducos, Lothar Rottmann, Julian D. Wills, Marcus Manecki

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In the last decades, inductively coupled plasma mass spectrometry (ICP-MS) has become the method of choice for researchers in order to gain deepest insights into fundamental principles of life and environment. However, even if this technique allows, due to its high sensitivity and linearity, for the quantitation of nearly all elements of the periodic table from the lowest ng/L range up to several mg/L, some drawbacks still need to be overcome.

One of the major disadvantages of ICP-MS are isobaric, sometimes polyatomic, interferences, which can be eliminated by an increase of either the physical or the chemical resolution of an ICP mass spectrometer. Here, false positive results can be avoided and best limits of detection can be obtained. Linked with this issue, there is another disadvantage, which gives room for improvement: the time needed to set-up and validate methods, especially if advanced techniques like ion chromatography, laser ablation or nano-particle characterization are involved. The more complex the technique is, the more parameters need to be adjusted, especially for multi-element methods in complex matrices.

Here, we present new, easy to use techniques based on improved interference suppression, which allow obtaining lowest limits of detection even for challenging matrices and allows scientists to focus on their research.

11:30am - 11:40am

VS-VENDOR SESSION: 6

Topics: Elemental analysis

Keywords: Speciation, reference, arsenic, selinium, chromium

Development of Reference Materials and Methodology for Inorganic Speciation Analysis

Patricia L Atkins

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Elemental species have always played an important role in many biological and ecological processes. Over the years, analysts have realized that efficient means of elemental speciation analysis was needed to correct identify hazardous concentrations of dangerous species such as methyl mercury and hexavalent chromium. Technology over the last decade has introduced new instruments such as LC-ICP-MS as a tool in this speciation analytical arsenal. The use of new methodologies must be validated in many industries to become a standard for use. To this end reference materials are developed and characterized to meet the needs of the analytical community. This presentation will discuss the background history and methodologies of speciation with a focus on the validation and analysis of certified reference materials for common inorganic species such as arsenic, selenium and chromium.

11:40am - 11:50am

VS-VENDOR SESSION: 7

Topics: Sample introduction and sample preparation, Elemental analysis
Keywords: naphtha, trace elements, ICP-AES, ICP-OES

Direct Determination of impurities in fuels and naphtha – A new approach using pneumatic nebulization and the ARCOS MultiView ICP-OES

Dirk Wüstkamp
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The analysis of trace metals in naphtha is an important application in the petrochemical industry, especially for the cracking of hydrocarbons. The presence of trace metals can impact this process as well as poison the often expensive catalysts used.

Another application is the control of trace elements in fuels (e.g. gasoline, diesel, biodiesel and ethanol fuels), since they can negatively affect the catalytic converters of the gas treatment systems or cause carbon deposits in the fuel injection system as well as the combustion chamber.

For this reason the elements have to be detected at µg/kg level.

In the past the analysis of organic solvents by ICP-OES was often considered problematic, even more so when the solvents were of high volatility. When volatile compounds such as naphtha are introduced into an ICP, the drastically enhanced sample transport efficiency leads to high plasma loads, instabilities and may even extinguish the plasma.

The new ARCOS Multi View ICP-OES handles a large variety of volatile petrochemical samples without dilution or a cooling device. Low, µg/kg limits of detection for 25 elements in diesel, ethanol, gasoline and naphtha as well as measurements over several hours, which exhibited excellent stabilities will be presented.

11:50am - 12:00pm

VS-VENDOR SESSION: 8

Topics: Sample introduction and sample preparation

Keywords: biological samples, sample preparation, method development

Method development for the analysis of biological samples by ICP-MS – sample preparation methods and instrument features

Rene Chemnitzer, Sebastian Wuenscher, Peio Riss, Iouri Kalinitchenko, Andrew Ryan

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The analysis of body fluids is an increasing area of application for ICP-MS. The interest affects more and more elements with different concentration levels in urine, serum, plasma or whole blood samples. The simplest preparation is to analyze directly, although the high matrix of biological samples usually exceeds the total dissolved solids (TDS) limit that an ICP-MS can routinely analyze long term. This requires a careful sample preparation procedure prior to analysis. Even the pH of the final sample to be analyzed is important in determining which elements can be precisely measured. Therefore, the question often asked “What is the best way to prepare biological samples for analysis by ICP-MS”.

Different approaches are discussed in the literature[1] and adopted in laboratories. The sample preparation methods evaluated include:

1. Complete acid digestion using closed-vessel microwave digestion
2. Acidic dilution in 0.5%HNO_3, 1% Propanol, 0.1% Triton X-100 and 200ppb Au
3. Alkali dilution in 2% NH_4OH, 2g/L EDTA, 1% Propanol , 0.05% Triton X-100 and 200ppb Au

A review of the data demonstrates that all three methods achieved excellent recoveries, well within the certified range for most elements.

Propanol is added to buffer the effects of carbon on As and Se due to the variable organic content in biological samples. The presence of carbon is known enhance the signal due to an increase in As and Se ion formation. The addition of a small flow of nitrogen gas has also been shown to influence ionization of As and Se within the ICP. As part of this study, the effect of adding nitrogen gas to the plasma was studied and found to be beneficial for both As and Se. A small flow of approximately 60mL/min nitrogen gas added to the argon auxiliary gas line not only enhances the signal, but was also found to buffer the effects of variable carbon content. This is evident in the similar results obtained when adding propanol only and nitrogen only.

The organic content in biological samples does also contribute to interference formation on e.g. Chromium ($^{40}Ar^{12}C^+$ on $^{52}Cr^+$). Thus an efficient interference removal is crucial to obtain correct results. Interference reduction by collisions with e.g. Helium does always influence the sensitivity on analyte ions as well. If a voltage is applied to the skimmer cone of the ICP-MS interface, the ion focusing properties are improved significantly resulting in a dramatic increase in sensitivity. Studies on the method development for the analysis of Chromium in blood samples prove the enhanced performance using the skimmer bias and results will be presented within the presentation.

12:00pm - 12:10pm

VS-VENDOR SESSION: 9

Topics: Elemental analysis

Keywords: Beer analysis, ICP-MS, ICP-OES, LCMS, heavy metals, pesticides, glyphosate

Determination of contaminants in beer using ICP-MS spectrometry

Uwe Oppermann[1], Jürgen Schram[2], Ludivine Fromentoux[3], Jan Knoop[1]

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The German Beer Purity Law of 1516 makes beer one of the best analyzed food products with the highest standards regarding quality, freshness, appearance and flavor.

According to this law, beer is allowed to contain hops, malt, yeast and water as ingredients. Of course, beer also contains major B vitamins, bitter substances and minerals and trace elements (e.g. Ca, Na, Mg and Zn) that are important for human nutrition. However, undesirable substances such as pesticides and heavy metals (for instance Cd, Pb, Hg, Sb and As) can be found as well, mostly as contaminants in brewing water and grains.

The quality standards for beer analysis are defined by the *Central European Commission* for brewing Analysis (*MEBAK*) and the European Brewery Convention (EBC) which is an organization representing the technical and scientific interests of the brewing sector in the European countries.

These regulations include the principles and proceedings for the analysis of raw materials, semi-finished goods, by-products and finished products, additives and technical supplies, containers and packaging materials with the aim of standardization, primarily in the field of breweries and malting industries. The technical analysis methods of MEBAK have been published in several application books, including the determination of elements like copper, zinc, sodium, potassium, calcium and more, anions such as nitrate and sulfite as well as organic components such as ethanol, glycerine and others [1].

Nowadays, the health effects of trace elements and the maximum concentration of trace elements in beers are continuously controlled. The determination of trace metals in beers is relevant, because they might be essential or toxic in the human body and they also have an influence on the brewing process. The element distribution however is showing significant differences based on the natural sources of soil, water, cereal, hops, and yeast and finally through anthropogenic sources such as environmental pollution and agricultural treatment by fertilizers, pesticides and fungicides.

Last not least, the metal content in beer can be influenced during production, beer processing, conservation and bottling, which is more than expected, as during the beer making process the raw products and processed products are often in long contact with various materials, such as stainless steel, copper, glass bottles and other equipment and many more.

For simultaneous multi-element analysis at ultra low concentration levels, ICP-MS is the preferred quality control tool. Experimental work has been done on the Shimadzu ICPMS-2030 with a variety of beers and analytical results will be presented.

References:

77[1] Pfenninger, H.: Brautechnische Analysenmethoden (1996)

12:10pm - 12:20pm

VS-VENDOR SESSION: 10

Topics: Sample introduction and sample preparation

Keywords: microwave digestion

How do microwaves support an Analytical Chemist in his daily work?

Linda Kuenstl

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Current Microwave Digestion systems provide much more than accelerating acid digestion. Of course the acid digestion is brought to perfection with several configurations from high temperatures (300 °C) to high throughput (> 40/h) applications, from high sample volumes (> 50 mL) to low sample volumes (< 50 µL), from high sample weights (g-range) to low sample weights (mg-range). Additionally, Microwave-induced Oxygen Combustion supersedes oxygen bombs for the determination of non-metal elements in combustible samples. Lowest blank levels can be achieved by using diluted instead of concentrated acids in Microwave-assisted UV-digestion or Microwave-induced Oxygen Combustion. With the help of microwave irradiation samples can be concentrated prior to the acid digestion, and acids can be evaporated afterwards. The extraction for speciation analysis can be done in a microwave system as well as providing reaction parameter recording for high reproducibility, speeding up the process and increasing the extraction efficiency. The self-made synthesis of standards becomes a topic when researching on speciation. In this case microwave reaction instruments accelerate the synthesis time from sometimes days down to minutes. During this talk the variety of applicable microwave support in laboratory work will be presented and application examples will be given.

SPEC-OL 2: SPECIATION - GENERAL SESSION 2

Time: Tuesday, 21/Feb/2017: 3:40pm - 4:40pm

Location: ARLBERG-well.com NORTH HALL
Session Chair: Maria Montes Bayón
Session Chair: Anna Maria Rathgeb

3:40pm - 3:50pm

SPEC-OL 2: 1

Topics: Application of speciation analysis, Environmental sciences
Keywords: Pilot Whales, Mercury, Speciation, detoxification

Hg detoxification in organs of Pilot Whales

Eva M. Krupp[1], Zuzana Gajdosechova[1], Mohammed Lawan[1], Urgast Dagmar[1], Brownlow Andrew[2]
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Long finned pilot whales are common in waters around the coast of Scotland. Pilot whales are known to mass strandings, from reasons largely unknown to science.

In recent years, 3 pods of pilot whales were stranded on the shores of Scotland, and in cooperation with the Scottish Marine Animal Stranding Scheme (SMASS), we had the opportunity to get a vast amount of samples of inner organs (liver, kidney, muscle, blubber), and more important several brains, from one pod of 21 whales stranded in Fife, South Scotland, with an age distribution from 1 to 36 years of age. This gave us a rare opportunity to analyse the organs of the whales through life time and access bioaccumulation patterns.

In this talk we will highlight outcomes of the analysis, in the light of detoxification strategies in marine mammals with a focus on mercury.

3:50pm - 4:00pm

SPEC-OL 2: 2

Topics: Elemental analysis, Application of speciation analysis, Environmental sciences

Keywords: iodine, seaweed, risk assessment, speciation, bioavailability

Iodine in seaweed - occurrence, speciation, bioavailability and risk assessment

Jens J. Sloth, Rie R. Rasmussen, Susan L. Holdt, Max Hansen

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Seaweed is the common term for marine macroalgae plants, which may be divided into green, red and brown algae types. There is an increased interest to increase the exploitation of marine macroalgae for commercial purposes including the use in relation to food and feed production. Certain seaweeds have a great potential to accumulate various trace elements and contain consequently relatively high levels of both essential and toxic elements. Seaweed can even be used for bioremediation purposes in order to remove trace elements from the environment.

The concentrations of iodine in seaweeds vary highly between the different types of seaweed. In green and red algae concentrations in the lower mg/kg are typically reported, whereas in certain brown algae concentrations in the g/kg range (dry mass) can be found. These very high levels raise concern about food and feed safety when brown algae are used consumed by either humans or animals. No maximum levels for iodine in seaweeds (or other types of food and feed) have been established in the legislation in EU. For humans an upper tolerable level at 600 µg/day has been established (EU SCF, 2002), hence consumption of as low as 100 mg of certain seaweeds would lead to an exceeding of this guideline value.

There is a need for a better documentation of the iodine levels in seaweeds and further knowledge on the biological and environmental factors that may influence the concentration levels (e.g. seaweed type, location and season). Furthermore, the speciation of iodine may also be an important parameter to take into account when assessing the safety of seaweed food and feed applications.

The present lecture will include:

i. examples of the use of seaweeds in various food items

ii. examples of the determination of iodine and iodine compounds in seaweed samples by (HPLC-)ICP-MS

iii. discussion of the results obtained in relation to food and feed safety assessment.

Reference:

European Commission, Opinion of the Scientific Committee on Food on the Tolerable Upper Intake Level of Iodine, 2002

4:00pm - 4:10pm

SPEC-OL 2: 3

Topics: Elemental analysis, Application of speciation analysis, Metallomics, Environmental sciences
Keywords: Arsenic species, fungi, accumulators, ICPMS, HPLC

Not only seafood can contain a lot of arsenic

Simone Braeuer[1], Jan Borovička[2], Walter Goessler[1]

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Recent research on arsenic and its species has mostly been focused on the marine environment. High arsenic concentrations have been found in fish and algae, and some new natural arsenic species have been detected there, including arsenolipids and, most recently, arsenic-containing phosphatidylcholines.

In the terrestrial environment, most arsenic research is being dedicated to rice, which has also led to the establishment of new health safety regulations by the European Union to ensure low levels of inorganic arsenic in rice and rice based products. However, when talking about the total arsenic concentrations, some terrestrial organisms can contain much higher levels than rice or even seafood: fungi. Depending on the fungal species, up to several thousands of mg As/kg dry mass have been detected.

Not only the total arsenic concentrations in fungi are incredible, but also the arsenic speciation is remarkable. Compounds like arsenobetaine or arsenocholine have already been detected in serveral species in the 1990s. These compounds can hardly be found anywhere else in the terrestrial environment in significant amounts. During our recent studies on arsenic accumulating mushrooms, other more unusual arsenic species were also detected. Again, depending on the fungal species, the arsenic speciation can vary significantly. To elucidate this phenomenon, we collected different mushroom species in the Czech Republic and Austria. We determined the concentrations of arsenic and also around 30 other elements with inductively coupled plasma mass spectrometry (ICPMS). Next, we extracted the arsenic species from the samples and analyzed the extracts with high performance liquid chromatography (HPLC) coupled to ICPMS. We used anion-exchange and also cation-exchange chromatography to check for some commonly found arsenic compounds like inorganic arsenic, methylarsonic acid and arsenobetaine, but other more unusual arsenic species were detected as well. Quantification was carried out by using external calibration with pure arsenic species standards. We tried to identify the chemical form of some of the more abundant unusual arsenic signals with different techniques, including size-exclusion chromatography and molecular mass spectrometry.

Future investigations of more mushroom samples will help us to gain valuable insight into the still unclear biotransformation processes of arsenic in nature, especially in fungi.

This joint project is funded by the FWF, project number I 2352-B21.

4:10pm - 4:20pm

SPEC-OL 2: 4

Topics: Application of speciation analysis

Keywords: iodine, speciation, stability of compounds

Stability of iodine species determined by HPLC-ICP-QQQ after enzymatic extraction

Ana Jerše[1,2], Ana Kroflič[1,2], Vekoslava Stibilj[1,2]

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Iodine is one of the essential elements for humans and animals. It is important for normal growth and development since it is in a part of thyroid hormones. The main source of iodine for humans is iodized salt, but due to the possible health problems associated with excessive salt consumption, WHO recommended a reduction of the amount of salt in nutrition. Therefore we need to search for alternative ways of introducing iodine into food to prevent repeated increase of iodine deficiency disorders.

Enrichment of various plant species with iodine could be an effective way of improving the iodine nutrition status. However, besides the total iodine concentrations, iodine compounds have to be determined due to the possible differences in bioavailability of diverse compounds.

There is a great lack of information about methods for iodine determination in terrestrial plants. Therefore our aim was to develop a method for iodine speciation by HPLC-ICP-QQQ using anion exchange column after the enzymatic extraction.

40 mg of enzyme (pancreatine, protease, amylase or lipase) were mixed with 7 mL of 0.2 M KH_2PO_4/0.2 M NaOH buffer with pH = 8. Standards of I^-, IO_3^-, monoiodothyrosine (MIT) and diiodothyrosine (DIT) were added into the vessels, except blanks, so that final concentration of each was 200 ng/mL. The extraction was performed using water bath with longitudinal shaking for 12 hours at 25, 37 and 50 °C and for 24 h at 50 °C or ultrasonic bath for 12 h at 50 °C (37 kHz, 70 % of power). After the extraction samples were filtered and frozen until analyzed.

The results showed good stability of three of the standards, I^-, MIT and DIT. Although a small peak of MIT was present when DIT was the only standard added, the ratio between peaks for DIT and MIT were constant, so we assume a small amount of MIT is present in the original standard. However, the peak for IO_3^- was present only when extraction was performed in buffer without enzyme or when IO_3^- was added just before injection. When the extraction was applied to the solution of buffer, IO_3^- and enzyme, regardless to the enzyme and temperature, time and bath used for the extraction, IO_3^- was interconverted to I^-.

Therefore we concluded that with the described method MIT, DIT and total inorganic iodine in the form of iodide can be determined. In addition, we found no differences between four different enzymes when applied to standards in buffer solution containing enzymes neither when different temperatures, time nor bath were used.

4:20pm - 4:30pm

SPEC-OL 2: 5

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: Lithium Ion Battery, Gas Chromatography, Organophosphorus Speciation

Speciation Analysis of Organophosphorus Aging Products of Lithium Ion Battery Electrolytes by means of GC-ICP-SF-MS

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The most important but as well the most delicate part of a state-of-the-art lithium ion battery is the electrolyte; especially safety issues have to be investigated in the rising times of the electromotive industry. The electrolyte therefore has to meet challenging requirements with regard to performance, cycling stability and safety. Lithium hexafluorophosphate ($LiPF_6$) in combination with a mixture of different organic carbonates is the outcome of long-term research and common in commercial applications. Since the exclusion of moisture is nearly impossible, hydrolysis reactions of the strongly hygroscopic conductive salt occur during operation of the battery leading to chain reactions of the electrolyte and, eventually, to failure of the system. Not only hydrofluoric acid is one of the toxic by-products of this decomposition route but also organophosphorus compounds with structural similarity to chemical warfare agents (CWA) like soman[1] are formed. Though only present in small amounts in laboratory scale cells, the quantity becomes significant with regard to electromotive upscaling of the battery system.

Since no molecular standards for these highly toxic compounds are commercially available, quantification was performed using a high resolution SF-ICP-MS after separation of compounds with a gas chromatograph (GC). Medium resolution (4000) was sufficient to detect the phosphorus signal and to exclude polyatomic interferences. For the identification of compounds the setup was extended with a parallel GC-high resolution/accurate mass (HR/AM)-MS; with the same setup of both GC systems identification could be performed by the exact masses of the analytes. Finally, an instrument setup consisting of two high resolution hyphenation systems could be developed that is capable of performing both qualitative and quantitative analysis.

[1] Silver, S. D., *J. Ind. Hyg. Toxicol.*, **1948**, 30(5), *307-311*.

4:30pm - 4:40pm

SPEC-OL 2: 6

Topics: Isotope ratio analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis, Environmental sciences

Keywords: post-column dilution analysis, ICP-MS, Speciation, Ultra Trace Analysis, Technetium

New Calibration Techniques for ICP-MS for the Speciation and Ultra Trace Analysis of Technetium

David Clases[1], Marvin Birka[1], Michael Sperling[1,2], Uwe Karst[1]

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Isotope dilution analysis (IDA) has become a powerful internal calibration technique for ICP-MS for the highly precise and accurate determination of elements with at least two stable isotopes. However, monoisotopic elements are excluded from IDA and the calibration of many radioactive isotopes is cumbersome and expensive, since often neither elemental standards nor enriched standards are available. Technetium (Tc) is one of these monoisotopic elements inaccessible by conventional calibration methods.

^{99}Tci s a nuclide, which is generated in high amounts in nuclear waste as a result of the neutron induced fission of ^{235}U in nuclear power plants. The present abundance of ^{99}Tc in the environment is almost exclusively the result of anthropogenic contamination resulting from processes like nuclear weapon testing, reprocessing of spent nuclear fuel and waste disposal. Due to a long half-life of 214,000 years, a high mobility and a high fission yield, ^{99}Tc is considered to be the most important radionuclide in risk assessment of radioactivity in the environment, as well as in decommissioning nuclear facilities and in the management of nuclear waste. It is moreover considered to be an important contributor to the future collective dose to the population. Yet, appropriate methods for the determination in environmental samples are not available. Furthermore, ^{99m}Tc is widely used as contrast agent for medical diagnostics. Due to low concentrations and a lack of standards, a quality control and tracer accreditation in terms of quantification, and determination of the species specific activity is impossible with current methods.

In this work, a new quantification technique named isobaric dilution analysis (IBDA) is introduced as a new calibration tool for the monoisotopic occurring Tc. It uses the fact that conventional mass analysers for ICP-MS cannot distinguish between two isobaric isotopes of different elements. Therefore, Tc samples were spiked with a Ru solution, exhibiting an isobaric isotope with *m/z* 99. Similar as for IDA, monitoring the isotope ratio allows a more precise calibration of Tc. However, element-specific responses were considered in order to obtain accurate concentrations. A crucial advantage of this method is its capability to access the calibration of transient signals when used in a post column approach. First, this approach was used to conduct speciation analysis in Tc-based contrast agents. Here, ^{99}Tc species could be separated and quantified by means of IBDA-LC-ICP-MS and could subsequently assigned to specific structures by means of LC-ESI-HRMS. This allows an on-side quality control as well as a crucial improvement in the accreditation of novel tracer. Secondly, the approach enabled the determination of ^{99}Tc in water samples by means of online extraction chromatography with post column IBDA, revealing a measureable input of ^{99}Tc into the environment due to nuclear diagnostic facilities.

SPEC-OL 3: SPECIATION - GENERAL SESSION 3

Time: Tuesday, 21/Feb/2017: 5:20pm - 7:20pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Maria Montes Bayón

Session Chair: Anna Maria Rathgeb

5:20pm - 5:30pm

SPEC-OL 3: 1

Topics: Application of speciation analysis

Keywords: Speciation, Ion Chromatography, Gas Chromatography

The Modern Toolbox for Speciation Analysis: Getting Ready for Routine Application

Daniel Kutscher, Shona McSheehy Ducos

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Modern laboratories using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) perform a wide range of analytical tasks; however, in many cases it may be impossible to make judgments regarding toxic risk based on the determination of the concentration for a given analyte alone. In these cases, it is necessary “to identify and measure the quantities of one or more individual chemical species in a sample”[1] – in other words, speciation analysis must be performed.

The toolbox for performing speciation analysis contains a variety of different techniques, all of them having their related advantages and drawbacks. The selection of the appropriate technique depends on which elements should be analyzed, and hence the chemical and physical properties of the expected species, for example charge state, polarity or volatility. Due to the ionic nature of the most commonly investigated species, for example, As or Se, Ion Chromatography (IC) hyphenated to ICP-MS (IC-ICP-MS) is normally the method of choice. Methods based on this separation technique have meanwhile found their way into routine screening of for example food stuff such as rice.

Whereas hyphenation of techniques based on liquid chromatography is straightforward, the hyphenation of Gas Chromatography (GC) to ICP-MS is more challenging, as species are separated at higher temperatures, and need to be transferred to the ICP-MS through a heated transfer line in order to avoid condensation and hence sacrifice chromatographic resolution. However, for some species, such as alkylated derivatives of Tin, methods based on gas chromatography are significantly better when it comes to detection limits. A newly developed transfer line for the hyphenation of GC to ICP-MS (both quadrupole based and high resolution) will be shown in this presentation that greatly simplifies the general setup and the daily operation.

This presentation will highlight that is has never been easier to utilize hyphenated techniques in routine analysis. Dedicated solutions for integrated hardware control and simplest method development are key for solutions for routine application. However, modern technology to remove or eliminate spectral interferences is equally important and will also be highlighted.

1 IUPAC definition of Speciation Analysis

5:30pm - 5:40pm

SPEC-OL 3: 2

Topics: Application of speciation analysis

Keywords: Arsenic, seafood, seaweed, speciation

Speciation analysis of arsenic in seafood and seaweed based on stepwise extraction of water-soluble and non-polar species

Mesay Mulugeta Wolle, Sean D. Conklin

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Seafood and seaweed are major sources of dietary exposure to arsenic. Reports have shown that some of these foodstuffs contain inorganic arsenic, which is a Class I carcinogen. The toxicity and potential food safety concern of arsenosugars and arsenic-containing hydrocarbons, which are common in certain groups of these products, are currently in debate. Numerous methods are reported for arsenic speciation analysis in seafood and seaweed; however, most were optimized for only a few arsenicals in specific groups of samples. In the present study, methods were developed through rigorous evaluation of critical experimental conditions taking into account the need for methodologies that address the matrix and species variations in these products. Extraction solvents including water, organic solvents, water-organic mixtures as well as acidic, basic and enzymatic solutions were evaluated based on their efficiency in extracting arsenic from a wide range of matrices and their effect on the stability of arsenicals. Stepwise extraction of water-soluble and non-polar arsenic using hot water and a dichloromethane-methanol mixture, respectively, was found to be sufficiently quantitative while maintaining the integrity of arsenic species. The water-soluble arsenic was speciated by anion and cation exchange liquid chromatography–inductively coupled plasma–mass spectrometry (LC-ICP-MS) methods optimized in this study. Analysis of extracts required no further manipulation except filtration and dilution in water. At the current stage of this project, non-polar arsenicals are collectively determined after evaporating the organic extractant and digesting the residue in acid. The optimization and single-laboratory validation of the extraction and chromatographic methods, and their application to speciate arsenic in samples and reference materials of fish, crustaceans, mollusks and seaweed, will be discussed.

5:40pm - 5:50pm

SPEC-OL 3: 3

Topics: Elemental analysis, Application of speciation analysis, Environmental sciences
Keywords: arsenic, particulate matter, HPLC-ICPQQQMS, speciation

Determination of Arsenicals in Atmospheric Aerosols by HPLC-ICPQQQMS

Stefan Tanda[1], Oliver Steiner[1], Jitka Hegrova[2], Roman Licbinsky[2], Walter Goessler[1]

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Arsenic is ubiquitous in the environment and of special concern due to its varying toxicity depending on the chemical form and oxidation state present. Since air represents an important route of dispersion, arsenic in the atmosphere and especially particle-bond arsenic in the form of airborne particulate matter might be potentially harmful. Only limited knowledge exists about volatile arsenic species in the air surrounding us. Two types of volatilization pathways are responsible for arsenic present in the atmosphere – a hot temperature and a low temperature volatilization pathway, both including different sources (e.g. volcanoes, fossil fuel combustion or arsenic volatilization by bacteria and fungi). Arsine and its methylated forms are oxidized by microorganisms in the soil and by UV-light in the atmosphere to their corresponding non-volatile species arsenite, arsenate, methylarsonate, dimethylarsinate and trimethylarsine oxide. It is for this reason that volatile arsenicals could be determined via their corresponding non-volatile species in particulate matter (PM) by HPLC-ICPMS after extraction.

Therefore, airborne particulate matter samples (PM_x samples (x = 10, 2.5 and 1.0 µm) and samples from an electrical low pressure impactor, which collects particles in 14 size fractions in the range from 17 nm to 10 µm) are collected at sites with different geogenic and anthropogenic arsenic inputs. For the determination of the total arsenic content, samples are digested in a microwave assisted autoclave with nitric acid. For quality control, suited certified reference materials (CRMs) are digested as well (e.g. NIST SRM 1648a Urban Particulate Matter). The digests are analyzed using a triple quadrupole ICPMS (Agilent 8800 ICP-QQQ). For arsenic speciation analysis, samples are extracted with water, followed by shaking/sonication and filtration. Subsequent analysis is done by HPLC-ICPQQQMS. A part of each extract is also digested to obtain information about the extraction efficiency.

Preliminary results from our first sampling campaigns indicate that inorganic arsenic is present mainly as arsenate and all organic arsenicals could be found in the different PM_x fractions, with trimethylarsine oxide as the dominant species in the aqueous extracts. The total arsenic concentration is typically around 0.5 ng As/m^3 air. Furthermore, we are able to see that the various arsenicals behave differently in particles with a diameter between 17 nm to 10 µm.

5:50pm - 6:00pm

SPEC-OL 3: 4

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Environmental sciences
Keywords: LIMS, Permafrost Sample, Space Research, Mars-relevant Analogue Material

Chemical analysis of Permafrost samples using LIMS

Andreas Riedo[1,2], Euan Monaghan[1], Marek Tulej[2], Peter Wurz[2], Pascale Ehrenfreund[1]

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The detection of extant life, or remnants of extinct life, on planetary objects is of high interest to current space research. Mars, due to its geologic and climatic history, is one of the most promising targets in the Solar System to find such traces of life. Various missions are planned in the near and mid-future, including ESA's ExoMars mission to explore the Martian surface and sub-surface. However, the detection of bio-signatures is extremely challenging, with problems ranging from the selection of the appropriate collection site to the application of sophisticated sample preparation techniques and instrumentation. Hence, continuous improvement of current collection and measurement techniques and development of new measurement technologies are of high importance for upcoming missions. In this contribution, we demonstrate the current measurement capabilities of our laser ablation/ionisation mass spectrometer (LIMS) system, designed for in situ analysis, and discuss measurements on Mars-relevant analogue material.

Measurements were conducted using the miniature reflectron-type time-of-flight LIMS system [1] designed for in situ analysis of the chemical composition of solids on planetary objects [2-3]. A femtosecond laser system (~190 fs, λ = 775 nm) was used for clean ablation and efficient ionisation of sample material (laser ablation crater in the range of ~10–20 µm in diameter) [1]. Parametric studies (laser irradiance and number of applied laser shots/position) were conducted on the sample material to investigate the most appropriate instrumental settings. In this contribution we present the chemical analysis of permafrost samples, highly abundant in biomass and collected at various depths through the sampling profiles, which was performed by the reported LIMS system, to elucidate the measurement capabilities of this instrument for such kind of samples. The impact of heat (3 h, 150 °C) on the sample composition was investigated as well; one important consequence of the heating was e.g. a significant reduction of carbon in comparison to other major/minor elements. These results will be compared in detail to that of non-heated samples.

[1] Riedo et al. (2013) J. Anal. At. Spectrom. 28, 1256 – 1269
[2] Tulej et al. (2015) Astrobiol., 15, 669 – 682.
[3] Neubeck et al. (2016) Int. J. Astrobiol., 15, 133 – 146.

6:00pm - 6:10pm

SPEC-OL 3: 5

Topics: Application of speciation analysis

Keywords: Arsenic Speciation, Wine, HPLC-ICP-MS

Arsenic Speciation in Wine by HPLC-ICP-MS - FDA EAM 4.10 Extension method

Jenny Nelson[1,2], Courtney Tanabe[1], Helene Hopfer[1,2], Susan Ebeler[1,2], Sean Conklin[3], Kevin Kubachka[4], Robert Wilson[4]

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A multi-laboratory validation (MLV) was performed to extend the FDA's Elemental Analysis Manual (EAM) method 4.10 (*High Performance Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometric Determination of Four Arsenic Species in Fruit Juice)* to include wine. Several modifications were examined to optimize the method for the analysis of dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), arsenate (As(V)), and arsenite (As(III)) in matrices of varying EtOH concentrations by HPLC-ICP-MS. The optimized method, which addresses issues with MMA enhancement, was used for the analysis of five wines of different styles (red, white, sparkling, rose, and fortified) by three laboratories. Additionally, the samples were fortified at levels of approximately 5, 10, and 30 µg kg^{-1} and analyzed in duplicate by each participating laboratory. The combined average fortification recoveries of DMA, MMA, and inorganic arsenic (iAs – the sum of As(III) and As(V)) in five samples for a total of n=30 per lab were 101%, 100%, and 101%, respectively. The total As concentrations of the 5 wines used for the MLV study were between 2.2 ± 0.1 and 15.3 ± 1.2 µg kg^{-1}. The concentration of As found in the form of iAs in these 5 MLV samples was between 1.2 ± 0.1 and 14.4 ± 1.0. Limit of detection (LOD) for this method for DMA, MMA, and iAs was 0.17 µg kg^{-1}, 0.15 µg kg^{-1}, 0.17 µg kg^{-1} respectively. The limit of quantification (LOQ) for DMA, MMA, and iAs was 1.3 µg kg^{-1}, 1.2 µg kg^{-1}, and 1.4 µg kg^{-1} respectively.

To further validate the method, 60 additional wine samples were analyzed. The results for QC samples included in the small-scale market basket study were similar to those from the MLV while covering a wider range of *in situ* arsenic concentrations. Also discussed in this presentation are efforts of shortening the 4.10 extension method to utilize a chromatographic separation of under 3 minutes per analysis.

6:10pm - 6:20pm

SPEC-OL 3: 6

Topics: Application of speciation analysis

Keywords: GC-ICP-MS, organophosphate pesticides, honey, QuEChERS

Gas chromatography coupled to triple quadrupole ICP-MS quantification of organophosphate pesticides in honey bee products after miniaturized QuEChERS extraction

David Munoz[1], Julio Landero[2], Joan Stevens[3], Jenny Nelson[3]

[1]Autonomous University of Yucatan, Merida, Yucatan, Mexico; [2]University of Cincinnati, Cincinnati OH, USA; [3]Agilent Technologies, Inc., Santa Clara, CA, USA; jenny_nelson@agilent.com

The use of an elemental detector as powerful as inductively coupled plasma mass spectrometry (ICP-MS) has impacted several areas of research by increasing detection power and decreasing interferences. The powerful ionization source allows compound independent quantification of most metals and metalloids at sub-ppb levels. However, some biologically and environmentally relevant elements like S, P and Se suffer from intense isobaric interferences from atmospheric and plasma related sources, compromising ICP-MS measurements at low concentrations. In recent years a technological breakthrough on elemental analysis was introduced with a triple quadrupole configuration ICP-MS (ICP-QQQ), which dramatically increases the capabilities of this analytical technique to quantify difficult elements by removing the interferences using very controlled chemical reactions in the collision/reaction cell. We use this state of the art new instrumentation to measure organophosphate pesticides in honey bee products with very good results. For this, a gas chromatograph (GC) was directly coupled to an Agilent 8800 triple quadrupole ICP-MS in MS/MS mode, to monitor the hetero atom phosphorous as internal elemental tag in organophosphate pesticides. A miniaturized QuEChERS extraction and clean up procedure was optimized for bee wax, propolis, comb and pollen for GC-ICP-MS/MS analysis, and the results show recoveries of 75-105% for eighteen commonly used pesticides. The specific detection of phosphorous improved the quality of the obtained chromatograms for some of the most challenging samples, with limits of detection of 10 to 50 ng g^{-1}. Real samples from different geographic origins were analyzed, and coumaphos was detected in three of them. This new approach can reduce the amount of toxic waste generated, by avoiding the stock of large amount of standards and its health hazard risks associated.

SPEC-OL 3: 7

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: ETV, ICP-OES, Speciation

Material analysis of solid fuels by ETV-ICP-OES – Speciation of Sulfur and Oxygen

Daniela Bauer[1], Thomas Vogt[1], Dirk Wüstkamp[2]
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Using Electro Thermal Vaporization (ETV) as a sample introduction technique for the ICP-OES, the sensitivity for material analysis applications can be considerably increased. The experiments conducted show one order of magnitude lower limits of detection can be achieved. With this, the sensitivity range previously reserved for the globular arc (which is not anymore available) and the glow discharge sector field mass spectrometry can be reached, which opens new fields of application for solid sample analysis for the ICP-OES.

Using ETV, the solid sample can be vaporized within a graphite oven with temperatures up to 3000°C and be introduced into to plasma by an argon/reaction gas stream as a dry aerosol. Particularly for samples difficult to digest, like solid fuels this approach is ideal. In only 2 minutes and without any samples preparation, analyses in the µg/kg range can be performed.

The accuracy and trueness of the developed methods were validated with the complete set of Argonne Premium Coals, covering the rank range from lignite to semi-anthracite and certified reference materials. The results are comparable with the element contents of established methods, like XRF, NAA and ICP-MS. It is shown, that the fast, direct solid sampling multi-element method ETV-ICP OES is proved to be a suitable alternative to labor intensive traditional methods for the direct determination of relevant elements for energetic and material use of energy resources.

Based on controlled thermal decomposition of coal in argon atmosphere it is possible to determine and quantify the different sulfur binding modes additional to elemental sulfur in coals. If the total sulfur in coal is already known (e.g. ultimate analysis) calibrating is not necessary. Nevertheless, the possibility of calibration was subject of the study. In addition to the calibration of sulfur with solid standard reference material (NIST SRM 1632d) the feasibility of the calibration with liquid standard solution was investigated and no significant divergence for the two calibration methods with different matrix according to the Student t-test was found.
In regard to validating the presented method both total sulfur and the species values of the complete collection from the Argonne Premium sample coal bank were reviewed. The analysis showed comparable results with the reported amounts in literature. The developed direct solid sampling method is time and cost effective and well suited for the fast characterization of sulfur species in coal. The method can be automated to a large extent and is applicable for processes accompanying analyses.
Additionally, the determination of the specific organic oxygen is under investigation.

ISO-PL: ISOTOPE RATIO ANALYSIS - PLENARY LECTURE

Time: Wednesday, 22/Feb/2017: 9:00am - 9:30am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

9:00am - 9:30am

ISO-PL: 1

Topics: Isotope ratio analysis

Keywords: multi-collector ICP-MS, isotope ratio, laser ablation, speciation

Current trends in high-precision isotopic analysis using multi-collector ICP-mass spectrometry

Frank Vanhaecke

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Multi-collector ICP-mass spectrometry (MC-ICP-MS) was commercially introduced in the 1990s as a dedicated tool for high-precision isotopic analysis. It offers practically the same level of precision as does thermal ionization mass spectrometry (TIMS) and is thus suited for studying and quantifying natural isotope ratio variations of metals and metalloids, resulting from the presence of a radiogenic nuclide produced as a result of the decay of a long-lived and naturally occurring radionuclide or the isotope fractionation accompanying physical and chemical processes. Next to a higher sample throughput and (somewhat) lower demands in terms of sample pretreatment, especially the higher ionization efficiency of the ICP ion source and its flexibility in terms of sample introduction owing to the robustness and operation at atmospheric pressure of that same ICP are important advantages of MC-ICP-MS.

During the past couple of years, researchers have been exploiting the latter advantages to an increasing extent and are using MC-ICP-MS in more “adventurous” contexts. New and less self-evident isotopic systems, even including those of non-metals such as Cl and Br, are being studied in various contexts. Efforts are made to simplify sample pretreatment procedures by (on-line) automation of the sample preparation approaches or by avoiding the traditional target element isolation all together. Laser ablation (LA) as a means of direct interrogation of solid samples is increasingly used in combination with MC-ICP-MS for bulk or spatially resolved isotopic analysis. In addition, also speciated isotopic analysis is emerging. Separation techniques, such as liquid or gas chromatography are coupled on-line to an MC-ICP-MS instrument with the aim of obtaining information on the isotopic composition of the target element in the various chemical forms in which it occurs.

All of this in turn calls for further improvement of the MC-ICP-MS instrumentation as the introduction of low amounts of sample material and/or the need for monitoring low-abundant species requires higher sensitivity. The latter is, e.g., accomplished via improved interface designs and the use of Faraday cup resistors with a higher Ohmic resistance. The use of alternate sampling introduction techniques also gives rise to the need of dealing with transient signals. This not only requires adequate data integration strategies, but also detectors with a sufficiently fast response.

In this plenary lecture, these current trends will be discussed using examples from the recent literature.

ISO-IL 1: ISOTOPE RATIO ANALYSIS - INVITED LECTURE 1

Time: Wednesday, 22/Feb/2017: 9:30am - 9:50am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

9:30am - 9:50am

ISO-IL 1: 1

Topics: Isotope ratio analysis

Keywords: isotopic analysis, isotopic tracing, geochemistry, cosmochemistry

New developments in isotopic tracing of trace metals in earth, environmental and planetary sciences

Mark Rehkämper

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The application of isotopic tracing to study material transport and system mass balances goes back to the 1930's. Such methods have found widespread application but are particularly common and important in earth, environmental and planetary sciences. Many key scientific advances were thereby driven by the interest to investigate novel sample types and isotope systems and enabled by new analytical developments. This presentation will review recent advances and trends in trace metal isotope tracing.

The meteorites that are studied by cosmochemists offer a particularly wide range of isotopic anomalies that can be exploited for tracing purposes. This includes effects of cosmogenic and nucleosynthetic origin, as well as radiogenic isotope anomalies from the decay of now-extinct short-lived radionuclides. Many studies thereby rely on the ability to resolve extremely small isotope effects with data that have uncertainties approaching ±10 ppm (2sd). Consequently, such research has spurred developments in analytical methods (i.e. sample preparation) and instrumentation and will particularly profit from further improvements.

The ability to conduct quick but robust and precise stable and radiogenic isotope analyses of trace metals, as afforded by MC-ICP-MS, the double spike technique and other innovations, has led to rapid and widespread adoption of such methods in earth sciences, and studies of 'non-traditional' stable isotope systems are hence a current mainstay of geochemistry. The diversity of applications, which range from investigations of the early Earth to trace metal cycling in the ocean, suggests that further innovative uses will arise in the future.

In particular, there is significant scope for interdisciplinary trace metal stable isotope research in life and medical sciences. Interest is still developing but such work promises to deliver new understanding of trace metal uptake and metabolism, which may be harnessed, for example, to support improvements in food safety or the development of diagnostic techniques for cancers. These applications typically involve analyses of much larger sample numbers than are common in geochemistry, so routine use will require more automation in sample preparation and enhanced availability of mass spectrometers for high precision trace metal isotope measurements. Such developments would also support more common use of high-sensitivity trace metal tracing studies with enriched stable isotopes, which are, for example, enabling environmental investigations of metal and metal-oxide nanomaterials at realistic exposure concentrations.

ISO-OL 1: ISOTOPE RATIO ANALYSIS - GENERAL SESSION 1

Time: Wednesday, 22/Feb/2017: 9:50am - 10:10am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

9:50am - 10:00am

ISO-OL 1: 1

Topics: Sample introduction and sample preparation, Isotope ratio analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis, Environmental sciences

Keywords: Perchlorate, Isotope, Seperation, MC-ICPMS

Development of δ37Cl isotope analysis by Ion Chromatography/MC-ICPMS and its application for studying biodegradation of perchlorate

Yevgeni Zakon[1,2], Ludwik Halicz[2,3], Zeev Ronen[4], Faina Gelman[2]

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Purpose: Perchlorate is a widespread environmental contaminant. It is primarily associated with releases of ammonium perchlorate in military related sites. Although it is a strong oxidant, perchlorate anion is very persistent in the environment due to the high activation energy associated with its reduction. In concentrations above the permitted level (30 µg/L) perchlorate is toxic for humans since it can affect thyroid gland functions. Microbial biodegradation of perchlorate is one of the possible treatment technologies for perchlorate removing. During biodegradation perchlorate is reduced to chloride through chlorate and chlorite formation. $\delta^{37}Cl$ isotope analysis may serve a helpful tool to trace this process in the environment. Until now $d^{37}Cl$ analysis was performed mainly by Gas Sourse – Isotope ratio Mass spectrometry or by TIMS and required a complex sample preparation procedure.

The present work we present a new on-line $d^{37}Cl$ isotope analysis in perchlorate by Ion Chromatography (IC)–MC-ICPMS. This method was applied for evaluation of $^{37}Cl/^{35}Cl$ isotope enrichment factor (ε_{Cl}) during microbial degradation of perchlorate in laboratory experiments in field study.

Methods: The method is based on separation of individual anionic species by IC followed by their direct isotope analysis by MC-ICPMS. Generally, $\delta^{37}Cl$ analysis in all anionic species (Cl^-, ClO_2^-, ClO_3^-, ClO_4^-) containing Cl can be performed during the same analytical run. Major isobaric interferences were reduced by using "dry" plasma conditions and applying sufficient mass resolution power ($\Delta M/M$ ~10000). Sample-standard bracketing technique was used for mass bias correction. Precisions in the range 0.3-0.4‰ were attained for analytes containing 1 µmol of Cl.

Results: The developed method for $\delta^{37}Cl$ isotope analysis allowed to attained sufficient precision for tracing the changes in perchlorate isotope composition during biological transformations.

Laboratory experiments with microbial cultures from the contaminated site showed significant chlorine isotope fractionation (ε_{Cl} ~14) in perchlorate during biodegradation. These results are in a good agreement with the data previously published in the literature.

Conclusion: IC-MC-ICPMS method for the $\delta^{37}Cl$ analysis shows a good performance and can be applied routinely for analysis of perchlorate and other chlorine containing anionic species. This method can be applied for tracing degradation of perchlorate in the environment.

10:00am - 10:10am

ISO-OL 1: 2

Topics: Isotope ratio analysis

Keywords: Multicollector ICP-MS, linear regression, Laser Ablation, Gas Chromatography

MEASUREMENT OF LEAD, STRONTIUM AND MERCURY ISOTOPE RATIOS BY MULTICOLLECTOR ICP-MS USING LINEAR REGRESSION IN COMBINATION WITH TRANSIENT SIGNALS

Jose Ignacio Garcia Alonso, Aida Reguera Galán, Mariella Moldovan, Silvia Queipo Abad, Pablo Rodríguez González

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Alternative data treatment procedures have been employed in multicollector ICP-MS isotope ratio measurements to improve the precision of the measurements. In this line, linear regression has been applied previously for the measurement of isotope ratios by Laser Ablation sampling [1], for trace element speciation in mercury fractionation studies [2] and also after a chromatographic separation of isobaric nuclides [3]. In this presentation we will try to demonstrate that the range of application of linear regression for Laser Ablation sampling and chromatographic separations can be extended to a) the internal correction of isobaric interferences of Rb on Sr, b) the determination of different isotopic forms of Pb in heterogeneous minerals and c) the evaluation of matrix effects on mass bias for improved Pb and Hg isotope ratio measurements.

For Laser Ablation we employ a dual inlet system in which the dry aerosol from the laser ablation system is mixed with a wet aerosol from a microconcentric nebulizer. In this way we can obtain a transient signal from the laser ablation chamber and combine it with a constant or a transient signal from the microconcentric nebulizer. A similar set-up is employed for the coupling of GC to the multicollector instrument. By selection of the element and signal type employed with the microconcentric nebulizer different corrections can be applied. For example, by generation of a transient signal for Rb in the microconcentric nebulizer the contribution of Rb to the Sr signal by laser ablation can be eliminated. So, this presentation will summarize the different application fields of this dual inlet system in multicollector ICP-MS.

[1] J. Fietzke, V. Liebetrau, D. Günther, K. Gürs, K. Hametner, K. Zumholz, T.H. Hansteen and A. Eisenhauer. *J. Anal. At. Spectrom.*, 2008, **23**, 955-961

[2] V.N. Epov,S. Berail, M. Jimenez-Moreno, V. Perrot, C. Pecheyran, D. Amouroux,. O.F.X. Donard, *Anal. Chem. 2010, 82, 5652–5662*.

[3] J.A. Rodríguez Castrillón, S. García Ruiz, M. Moldovan, J.I. García Alonso. *J. Anal. At. Spectrom.*, 2012, **27**, 611-618.

ISO-IL 2: ISOTOPE RATIO ANALYSIS - INVITED LECTURE 2 (AGILENT RISING STAR AWARD)

Time: Wednesday, 22/Feb/2017: 10:50am - 11:10am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

10:50am - 11:10am

ISO-IL 2: 1

Topics: Isotope ratio analysis

Keywords: isotope ratio analysis, MC ICP-MS, Mo, B, Sr, Pb, Ti

Multi-isotope tracers to investigate processes in river catchment systems: Selected application examples using B, Mo, Sr, Pb, and Ti isotope ratios assessed by MC ICP-MS

Johanna Irrgeher[1], Florian Dutschke[1,2], Anna Reese[1,2], Anika Retzmann[3], Tristan Zimmermann[1,2], Thomas Prohaska[3], Michael E. Wieser[4], Andreas Zitek[3], Daniel Proefrock[1]

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Environmental monitoring of complex ecosystems requires reliable sensitive techniques based on sound analytical strategies to identify the source, fate and sink of elements and matter. Isotopic signatures can serve to trace pathways by making use of specific isotopic fingermarks or to distinguish between natural and anthropogenic sources. The presented work shows the potential of using the isotopic variation of Sr, Pb (as well-established isotopic systems), Mo and B (as novel isotopic system) assessed by MC ICP-MS in water and sediment samples to study aquatic ecosystem transport processes. In addition, Ti isotopic signatures were assessed in TiO_2 nanoparticles to elucidate if Ti present in aquatic ecosystems can be related to different possible sources since TiO_2 nanoparticles (TiO_2-NPs) have been recognized as potential emerging environmental contaminants as they are used in many products of daily use (e.g. pigments, sunscreens and cosmetics), which results in their constantly increasing release to the environment.

The isotopic variation of Sr, Pb, Mo and B was determined in different marine and estuarine compartments covering the catchment of the German Wadden Sea and its main tributaries, the Elbe, Weser and Ems River. The varying elemental concentrations, the complex matrix and the expected small variations in the isotopic composition required the development and application of reliable analytical measurement approaches as well as suited metrological data evaluation strategies. Aquatic isoscapes were created using ArcGIS® by relating spatial isotopic data with geographical and geological maps. The elemental and isotopic distribution maps show large variation for different parameters and also reflect the numerous impact factors (e.g. geology, anthropogenic sources) influencing the catchment area.

The potential of using the isotopic composition of Ti in TiO_2 nanoparticles to differentiate between different nanomaterials was investigated by analysis of different commercially available TiO_2 products using solution-based MC ICP-MS including experiments to evaluate possible matrix effects originating from impurities (e.g. Ca, Cr, Mg, Al, Zr, Fe, Si, V) in the TiO_2-NPs as well as calculations of combined uncertainty budgets. The presented data shows for the first time the potential to differentiate between some of the individual TiO_2 nanoparticle products based on their individual isotopic composition.

ISO-OL 2: ISOTOPE RATIO ANALYSIS - GENERAL SESSION 2

Time: Wednesday, 22/Feb/2017: 11:10am - 12:00pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

11:10am - 11:20am

ISO-OL 2: 1

Topics: Sample introduction and sample preparation, Isotope ratio analysis

Keywords: sample preparation, isotope analysis, Sr, Pb, Nd

Optimization of a new fully automated sample preparation system for the isotopic analysis of Sr, Pb and Nd in sediment digests via MC ICP-MS

Tristan Zimmermann[1], Anika Retzmann[2], Johanna Irrgeher[1], Thomas Prohaska[2], Daniel Pröfrock[1]

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Today the German Bight is affected by various anthropogenic emission sources like ship traffic, off-shore construction and river derived pollution. Since little is known about inorganic pollutant concentrations or their distribution and variability in sediment provinces, there is an urgent need for new tools to trace inorganic contaminants and their transport processes. One possible analytical tool to accomplish these aims lies in the use of non-traditional stable isotopes. Sr, Pb and Nd are three elements with isotopic compositions that are intensively used in geochemistry for providing chronological information or tracing petrogenic processes. Further, they are also of specific interest in the field of marine geochemistry, as they will allow the tracing of the geological origin of sediments (Sr, Nd) as well as the tracing of anthropogenic emissions (Pb).

Over the past decades MC ICP-MS has matured to a powerful tool for the precise analysis of isotopic ratios in various kinds of environmental samples. Especially sediment and rock digests contain various matrix elements at high concentrations such as Si, Al, Fe and Ca. These have to be separated from the analytes of interest, since highly precise measurements of isotopic ratios via MC ICP-MS suffer from isobaric and polyatomic interferences as well as mass bias effects. For this purpose usually hand packed columns with different kinds of ion-exchange resins provided by various distributors are used. However, established separation protocols are often time-consuming and cost-intensive.

The *prepFAST-MC*®sample preparation system provided by *Elemental Scientific* (Omaha, Nebraska, USA) is a fully automated, column based chromatographic extraction system. The system enables the separation of the targeted analytes from matrix rich-samples using an analyte specific resin. Within this work I would like to present an optimized sample preparation protocol for the separation of Sr, Pb and Nd in sediment digests, based on the DGA resin (TrisKem International, Bruz, France).

The new, optimized method opens the possibility to separate three isotopic systems within a single analytical run, which helps to save time and effort compared to conventional (manual) separation techniques. The separation scheme can be applied to different sample matrices (sea water, soil extracts, sediment or rock digests) with high recovery rates (Sr >95%, Pb >90%, Nd >95%). Furthermore the DGA resin proved to be highly re-usable with low separation blanks. The optimized sample preparation protocol will be applied to sediment samples from the German North Sea and its main tributaries Elbe, Weser and Ems in order to generate isoscapes as basis for tracing the fate of sediments in the German North Sea catchment.

11:20am - 11:30am

ISO-OL 2: 2

Topics: Elemental analysis, Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Archaeometry and forensics

Keywords: Strontium, Isotopes, Diagenesis, Imaging, Solubility Profiling, LA MC ICP-MS, Archaeometry

Spectral Insights: Multi-dimensional approach to evaluate the diagenetic status of skeletal remains with respect to strontium isotope ratio measurements

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Strontium isotopic analyses by either TIMS or MC ICP-MS of in vivo incorporated environmental signatures (aka ‘biosphere fingerprint’) in human and animal skeletal remains have been widely used in anthropology and archaeology to trace residential changes, mobility or living conditions. Often the in vivo isotopic signature in bone and teeth is distorted by cumulative physical, chemical and biological alteration during burial which leads to exchange and/or addition of strontium from the burial environment (soil, water) – referred to as diagenesis. A well-preserved biogenic Sr signal is crucial for a reliable evaluation of historic migration (paths) using $^{87}Sr/^{86}Sr$-analysis. Thus, localizing biogenic areas and the spatial extent of diagenetic alteration is essential. So far there is no sufficiently satisfactory method to differentiate between diagenetically changed and biogenic regions in bones or teeth.

Herein we present the first results of the comparison between solubility profiling and bioimaging of archaeological bone to assess in vivo $^{87}Sr/^{86}Sr$ ratios of the biogenic material. Bioimaging was performed to spatially resolve the extent of diagenesis on bone cross-sections by simultaneous mapping diffusion profiles of $^{87}Sr/^{86}Sr$ ratios and the concentrations of Sr and elements of non biogenic origin (Ba, Pb, U) using laser ablation split stream ICP-QMS and MC ICP-MS [1].

In order to generate accurate $^{87}Sr/^{86}Sr$ ratios LA MC ICP-MS data need to be corrected for matrix-based polyatomic interferences such as Ca dimers and $CaPO^+/ArPO^+$-clusters in addition to Rb and correction for instrumental isotopic fractionation.

Preliminary results show diffusion gradients of trace elements originating from the repository material along with a change in the Sr isotopic composition which can be related to diagenetic processes. Subsequent imaging by ArcGIS allows the selection of areas of minor diagenetic alteration by using selected thresholds.

Within a pilot study initial measurements of the diagenetically altered bones were performed by near infrared hyperspectral imaging (NIR HSI). The preliminary results of the Principle Components Analysis of the HSI pictures already indicates differences correlated with the diagenetic changes identified by the biomapping, which shows the potential of NIR HSI in the context of monitoring diagenesis.

An Abstract with a similar content has been submitted to the conference 12. Symposium Massenspektrometrische Verfahren der Elementspurenanalyse und 25. ICP-Anwendertreffen (2016, Siegen, Germany).

[1] T. Prohaska, J. Irrgeher and A. Zitek, “Simultaneous multi-element and isotope ratio imaging of fish otoliths by laser ablation split stream ICP-MS/MC ICP-MS”, J. Anal. At. Spectrom., 2016, Advance Article, DOI: 10.1039/c6ja00087h.

11:30am - 11:40am

ISO-OL 2: 3

Topics: Isotope ratio analysis, Environmental sciences

Keywords: karst spring system, stable Mg isotopes, radiogenic Sr isotopes, geotracers

Water-rock interactions and fluid flow behavior within an alpine karst spring system (Johnsbachtal, Austria) - A multi-proxy approach including 87Sr/86Sr and δ26Mg signatures

Dorothee Hippler[1], Marcus Spitz[1], Jessica A. Stammeier[1], Oliver Nebel[2], Gerfried Winkler[3], Martin Dietzel[1]

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The Etzbach karst spring (Johnsbachtal, Gesäuse National Park, Austria) is sourced by a catchment composed of ore-bearing Devonian carbonates and overlying upper Ordovician volcanic rocks of the Graywacke Zone of the Eastern Alps. The spring displays several concave-aligned outlets within a distance of about 15 m, which are characterized by distinct physico-chemical parameters (e.g. EC ranging between 155 µS/cm and 392 µS/cm at different outlets) that are attributed to different flow components of the karst system. Former karst hydrological investigations have shown that the marginal outlets exhibit an authogenic matrix flow component, which is related to the ambient, karstified ore-bearing Devonian carbonate rocks. The central outlets are however recharged allogenicly by water through the conduit system, originating from the overlying upper Ordovician volcanic rocks of the Bärenkar cirque. The allogenic flow component was verified with tracer tests using fluorescein sodium. This different sourcing is thus an ideal natural laboratory to enhance the mechanistic understanding of chemical water-rock interactions within a karst system.

In the current study we investigated water samples from the different spring outlets. By applying a multi-proxy hydrogeological approach we aim (1) to trace the sources of aqueous components of this karst system, and (2) how they are influenced by ambient water-rock interactions and hydrological flow behavior. Traditional stable isotopes (δD_{H2O}, $\delta^{13}C_{DIC}$, $\delta^{18}O_{H2O}$) coupled with major element hydrogeochemical data of the spring waters indicate mixing of at least two different water types recharging the spring's outlets. The proportional contribution of respective endmembers is strongly related to the discharge, indicating a relation to sub-surface mixing processes. Strontium isotope ($^{87}Sr/^{86}Sr$) ratios range from 0.710061 to 0.712935 and cluster in two groups with more radiogenic signatures corresponding to spring waters of the central outlets. Magnesium isotopes ($\delta^{26}Mg$) range between -0.93 and -2.14 ‰ (DSM3), anti-correlating with $^{87}Sr/^{86}Sr$ ratios. We propose that the coupled Sr and Mg isotopic signatures in spring waters reflect source mineralogy of respective catchment areas of the karst spring system. Memory of source mineralogy preserved in combined radiogenic-stable isotope proxies may thus be a promising new tool for tracing subsurface water-rock interactions.

11:40am - 11:50am

ISO-OL 2: 4

Topics: Sample introduction and sample preparation, Isotope ratio analysis
Keywords: microsampling, Fe isotopic analysis, venous blood, capillary blood

Iron isotopic analysis of finger-prick blood via multi-collector inductively coupled plasma mass spectrometry after volumetric absorptive microsampling (VAMS)

Yulia Anoshkina, Marta Costas-Rodríguez, Frank Vanhaecke
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Several research groups reported on the use of the iron isotopic composition of whole blood or serum for achieving a more detailed understanding of human metabolism and/or in the context of early diagnosis and prognosis of diseases. However, simple and reliable sample collection and sample preparation methodologies, providing high sample throughput, are still lacking.

Volumetric absorptive Microsampling (VAMS) Mitra™ is a novel sampling technique that allows the straightforward collection of a well-defined volume of blood by dipping an absorbing hydrophilic polymeric tip into a drop of blood. In this work, the use of VAMS as a simple sampling technique in the context of the determination of the Fe concentration and the Fe isotopic composition in a finger-pricked blood sample was evaluated. A Thermo Scientific (Germany) Element XR sector field ICP-MS instrument was used for the target element quantification. Fe isotope ratio measurements were accomplished using aThermo Scientific Neptune MC-ICP-MS instrument. The extraction of Fe from the hydrophilic polymeric VAMS tip was studied using a variety of solvents. The Seronorm™ Trace Elements Whole blood L-1 reference material was used for optimization of the procedure. Fe concentrations were quantitative after direct extraction of the blood from the VAMS device with hot 50% nitric acid. For the isolation of Fe prior to isotopic analysis via MC-ICP-MS, a simplified and miniaturized procedure was developed using a 1 mL pipette tip as a chromatographic column.

Venous whole blood samples were used to validate the novel protocol for Fe isotopic analysis. Simultaneously collected finger-prick and venous blood samples were analysed to compare their Fe isotopic composition. No significant differences were found between the Fe isotopic compositions of venous and capillary blood (*t*-test). The proposed methodology substantially enhances the sample throughput and shows potential for routine use of Fe isotopic analysis for biomedical applications.

11:50am - 12:00pm

ISO-OL 2: 5

Topics: Isotope ratio analysis

Keywords: MC-ICP-MS, Europium, isotopic ratio, C-SSBIN, natural waters

Determination of europium isotope ratios in natural waters by MC-ICP-MS

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An analytical protocol for the accurate and precise determination of europium isotope ratio in natural waters is presented for the first time by using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Parameters affecting the separation of Eu based on a single-step column separation employing di(2-ethylhexyl) orthophosphoric acid (HDEHP) resin were investigated in detail. Matrix elements (*e.g.*, alkali, alkali-earth and some transition metals) were efficiently removed and the Eu was quantitatively separated from the other rare earth elements (REE) by sequential elution using gradient HCl concentrations (from 0.25 to 0.75 mol L^{-1}). Fractionation of Eu isotopes on the column was not observed, since quantitative europium recovery (101.2 ± 0.5 % mean and 1 SD, n = 3) was obtained (data based on 150 mL SLRS-6 river water CRM test portions spiked with 1.0 ng mL^{-1} Eu standard solution). A combined standard-sample bracketing with internal normalization (C-SSBIN) method was employed for the mass bias correction, wherein Gd added to both the sample and a solution was used as an internal standard. MC-ICP-MS method was validated by processing a 0.02 ng mL^{-1} Eu spiked SLRS-6 river water CRM using the proposed method and satisfying results ($\delta^{151/153}$Eu value of 0.01 ± 0.02 ‰; 1 standard deviation), relative to Eu standard solution, were obtained. No significant differences were found in the $^{151}Eu/^{153}Eu$ absolute ratios in the analyzed samples, which ranged from 0.915940 ± 0.000082 to 0.91619 ± 0.00021.

ISO-IL 3: ISOTOPE RATIO ANALYSIS - INVITED LECTURE 3

Time: Wednesday, 22/Feb/2017: 1:40pm - 2:00pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

1:40pm - 2:00pm

ISO-IL 3: 1

Topics: Isotope ratio analysis

Keywords: MC-ICP-MS, Isotopic analysis, Environment, hyphenation

Hyphenated MC ICP-MS methods for environmental research

Sylvain, Jean-Baptiste Bérail, David Amouroux, Emmanuel Tessier, Sylvain Bouchet, Julien Barre, Joana Cavalheiro, Zoyne Pedrero, Gilles Bareille, Christophe Pecheyran, Olivier, François-Xavier Donard

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Isotopic analysis with MC-ICP-MS are now widely used in environmental research essentially for discriminating sources and to improve our understanding of bio-geochemical cycle of elements.

The specific nature of the ionization source of the MC-ICP-MS allows the hyphenation to various types of specific sample introduction systems such as for example chromatography or laser ablation. These hyphenations are expanding the field of MC-ICP-MS applications and bring new dimensions to the isotopic analysis.

All these couplings are generating short transient signals that are challenging to deal with. The main issue is a loss in precision compare to continuous signal technique due both to poor counting statistic and slow response of the Faradays detectors. To overcome these limitations, specific data treatment strategies have been developed.

The compound specific isotopic analysis is an emerging approach providing the isotopic signature of different species of the same element. In this respect, the most noticeable analytical strategy is to couple gas chromatography to MC-ICP-MS. We will mainly focus on the typical case of Hg environmental studies to demonstrate the potential of such approaches.

Some coupling with MC-ICP-MS can also provide on line pre-concentration to decrease the minimum needed elemental concentration for precise isotopic analysis. In that frame, we developed hyphenations for both total and compound specific isotopic analysis of Hg at the $ng.L^{-1}$ range. We will present critical steps of technical validations as well as new results on rainwaters, seawaters and other low concentrated environmental samples.

When coupled to the MC-ICP-MS, the laser ablation is adding a spatial dimension to the isotopic analysis as well as high throughput capabilities. Some environmental applications using Sr and Pb isotopes will be also presented.

ISO-OL 3: ISOTOPE RATIO ANALYSIS - GENERAL SESSION 3

Time: Wednesday, 22/Feb/2017: 2:00pm - 2:40pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Heidi Goenaga-Infante

Session Chair: Anastassiya Tchaikovsky

2:00pm - 2:10pm

ISO-OL 3: 1

Topics: Isotope ratio analysis

Keywords: Copper isotopes, MC-ICP-MS, biological fractionation, copper metabolism, intestine

Copper isotopic fractionation in the intestine of transgenic mice

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Metabolic processes change the distribution of copper isotopes in biological materials and consequently can provide insight to metal trafficking pathways. Recent animal studies investigating copper isotopes have focussed on the entire system,[1,2] but there are limited studies that target a single organ to determine the variability in copper isotopic composition in either normal systems or those with disruptions to the copper metabolism. This study focusses on copper isotopic fractionation in the intestinal tract of transgenic mice. The intestinal tract is an ideal organ to study as it is the primary entry route of dietary copper into the body and the mechanisms of copper trafficking are reasonably well understood. Food travels from the stomach through the duodenum, jejunum, ileum, proximal colon and distal colon, respectively, before elimination from the body. This study investigated wild type mice, mice that lack the copper-binding prion protein, and a strain of mice where the copper-binding sites on the prion protein have been mutated and the protein is no longer involved in copper processing. The copper in the intestinal tissue was isolated via ion-exchange chromatography and the δ^{65}Cu values were measured using a Neptune MC-ICP-MS.

In all regions of the intestinal tract the cells were enriched in ^{65}Cu compared to the food source (0.31 ± 0.08 ‰), but the extent of the enrichment varied in each region. For example, in the small intestine of the wild type mice, the average δ^{65}Cu values of the duodenum (1.34 ± 0.47 ‰, n=5, 2sd) was greater than that of the jejunum (1.15 ± 0.52 ‰, n=5, 2sd), and the ileum (0.96 ± 0.40 ‰, n=5, 2sd). The other genotypes investigated showed a similar pattern and no genotype dependence on the isotopic fractionation was observed. In the large intestine of wild type mice, the average values of the proximal colon (1.16 ± 0.20 ‰, n=8, 2sd) and distal colon (1.33 ± 0.27 ‰, n=9, 2sd) indicate a significant change in copper processing at the junction between the small and large intestine. Contrary to the small intestine, there was a subtle dependence on genotype in the proximal and distal colon. The results clearly demonstrate that a significant fractionation occurs during the first interaction of dietary copper with the body and the extent of fractionation depends on the region of the intestinal tract.

1.) Balter et al, Metallomics, 2013, 5, 1470-1482

2.) Miller et al, JAAS, 2016, 31, 2015-2022

2:10pm - 2:20pm

ISO-OL 3: 2

Topics: Elemental analysis, Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Single particle analysis, Laser Ablation ICP-MS, Tandem analysis, LIBS, micro dried droplets

µ-Dried-Droplets as standards for Tandem single particle LIBS/LA-ICP-MS analysis

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The IAEA (International Atomic Energy Agency) can perform environmental sampling at the inspected nuclear facilities to assist in drawing conclusions about the absence of undeclared nuclear material or nuclear activities at the specified location. The size of the collected particles in the environmental swipe samples ranges from nm to several µm, containing Uranium in the pg-range. As these particles are collected together with large quantities of dust matrix, the analysis can be challenging. The low availability of suitable reference materials complicates the instrument tuning for the analysis and characterisation of single particles even further. Thus, optimised methods are required for satisfactory and comprehensive analysis of such particle samples.

In this work, a new approach using Tandem LIBS/LA-ICP-MS was used to analyse the geological matrix simultaneously with the Uranium isotopic composition. The knowledge about the composition of the sample matrix gained from the collected LIBS data, can improve the characterisation of the sample while not influencing trace element analysis using ICP-MS, which applies especially when employing only a single mass analyser. The broadband detection capabilities of a LIBS system alongside with the usually very high sensitivity for many crustal elements can help to identify and correct matrix induced effects in ICP-MS measurements.

A proof of principle study has been performed using µ-Dried-Droplet standards. This approach offers a flexible way to create in-house solutions for applications where appropriate reference materials are not available or cannot satisfy the analytical needs. The elemental and isotopic composition of the µ-droplet is governed by the applied liquid standard. This method allows to easily adapt the total amount of analyte and matrix composition in account to the needs of the current application thanks to the vast variety of available liquid certified reference materials.

In the presented study a variety of Uranium containing mock-up prepared by the above described µ-Dried-Droplets approach was investigated. Thereby prepared mock-up particles had a defined composition regarding their uranium content as well as matrix elements. Even with a quadrupole instrument a satisfactory determination of the uranium isotopic ratio and content as well as the matrix composition could be achieved, demonstrating the usability of this approach for single particle analysis.

2:20pm - 2:30pm

ISO-OL 3: 3

Topics: Isotope ratio analysis, Coupling techniques (chromatography, FFF, ETV, others)
Keywords: MC-ICPMS, Isotopic measurement, Nuclear samples, capillary electrophoresis, coupling techniques

Separation of Uranium and Plutonium by capillary electrophoresis coupled with MC-ICPMS for isotope ratio measurements

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Precise isotopic and elemental characterisation of nuclear spent fuel is a major concern for the validation of the neutronic calculation codes and waste management in the nuclear industry. The Nuclear, Isotopic and Elemental Analytical development Laboratory (LANIE) of the French Nuclear Agency has developped an analysis protocol for the characterisation of nuclear fuel samples using several purification steps. The first one, using ion exchange resin, leads to the chemical purification of uranium (U), plutonium (Pu) and fission products (including lanthanides (Lns) and minor actinides). The purified fractions of U and Pu are then analysed by multicollector mass spectrometric techniques. The LANIE attempts through various analytical developments to reduce the amounts of reagents, the amounts of samples required and the exposition of the analysts to radiation dose.

In this work we present the development of an electrophoretic separation of U, Pu and fission products which is directly coupled with a multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) for online isotope ratio measurements. A preliminary study was done using thorium (Th) as a chemical analog for Pu(IV). Four complexing agents were selected and tested over concentration and pH to evaluate their contribution on the separation selectivity. Acetic acid was found to be the most suitable complexing agent for the separation of U, Th and Lns. Ammonium salt was added to the electrolyte in order to stack in-situ the analytes using the principle of field enhancement. The instrumentation was adapted to be used in glove box in order to achieve the separation of U, Pu and Lns. In our optimised conditions Pu(VI) elutes before U(VI) which elutes before Pu(IV). The first measurements of uranium isotope ratio after electrophoretic separation directly coupled with MC-ICPMS will be presented. Using a spray chamber with two nebulisers, injections of standards were performed during the separation to correct for mass bias effects. Moreover, an isotopic drift induced by the separative technique was identified and distinguished from the drift induced by the detection system. The uncertainties obtained on uranium isotope ratios will be discussed and compared with those obtained with the previous analytical protocol.

2:30pm - 2:40pm

ISO-OL 3: 4

Topics: Isotope ratio analysis

Keywords: mercury, MC-ICPMS

Species-specific Hg isotope ratio measurements in fish by using HPLC and cold vapour MC-ICPMS: Insights into mass discrimination correction

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Mercury is considered a highly toxic, priority pollutant in the environment. Toxicity and transformation of mercury in natural settings depend on the chemical form the element. Species-specific isotope ratio data can be a useful tool in understanding biogeochemistry of mercury. High Performance Liquid Chromatography (HPLC) is a well-known means of separating methylmercury and inorganic mercury with high selectivity and without the need for derivatisation. Previous work on coupling of HPLC to MC-ICPMS for species-specific Hg isotope dilution analysis demonstrated that the major contribution to the overall measurement uncertainty was from isotope ratio measurements in transient mode.[1] For accurate and precise isotope ratio measurements of Hg species at low concentrations the use of HPLC coupled MC-ICPMS has significant challenges that need to be addressed. One of them is the need to ensure quantitative recovery of chemical species after their separation to avoid artificial isotope fractionation. A technique of cold vapour generation (CVG), used for Hg isotope analysis at low concentration levels, makes use of $SnCl_2$ as a reductant which is selective towards inorganic mercury. As a consequence, once methylmercury is separated from inorganic mercury the former needs to be broken down to inorganic form prior to isotopic measurements. Chromatographic procedures also rely on sulphur-containing mobile phase to achieve efficient separation of Hg species. Being a powerful complexing agent for mercury, sulphur interferes with quantitative release of mercury from solution in the CVG. This presentation will describe a newly developed methodology which enables efficient separation of inorganic mercury from methylmercury by HPLC followed by Hg isotope ratio measurements using by MC-ICPMS. Approaches for mass discrimination correction will also be discussed. The method has successfully overcome the aforementioned problems and allows reproducible Hg isotope ratio measurements in extracts of fish tissues with precision better than 0.2‰.

MT-PL: METALLOMICS - PLENARY LECTURE

Time: Wednesday, 22/Feb/2017: 3:20pm - 3:50pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Stephan Hann

Session Chair: Luis Gálvez

3:20pm - 3:50pm

MT-PL: 1

Topics: Metallomics

Keywords: metallomics, elemental speciation analysis, metallodrugs, metabolomics

It is metallomics, isn't it?

Luis Galvez Montano[1], Sarah Theiner[1], Michaela Schwaiger[1], Stephan Hann[2], Gunda Koellensperger[1]

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More than a decade ago, in analogy to the modern system level "omics" approaches the term metallomics was coined. As a consequence, biologically oriented method developments in atomic spectroscopy further on were not presented as elemental speciation approaches anymore, but were rather flagged as metallomic approaches. Regarding the comprehensive analysis of the metallome, compared to other "omics" disciplines, up to date there is no mature technological platform offering routine analysis of all metal species, hence the implementation of novel analytical strategies continues to be a topical research theme.

Evidently, the field of metallomics is embracing research beyond the pure analytical exercise focusing on the biological and biomedical role of metals. While in early days, the (bio)chemistry of the metals in biological samples was addressed by analysis of the metal species itself, recently, there was a paradigmatic shift towards interrogating the interaction of metals and metal species with other "omes". In the lecture emerging trends and focal points of innovation in metallomics will be critically discussed from the perspective of an analytical chemist.

MT-IL 1: METALLOMICS - INVITED LECTURE 1

Time: Wednesday, 22/Feb/2017: 3:50pm - 4:10pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Stephan Hann

Session Chair: Luis Gálvez

3:50pm - 4:10pm

MT-IL 1: 1

Topics: Application of speciation analysis, Metallomics

Keywords: nanostructured drugs, ICP-MS, cell uptake, platinum, iron

ICP-MS based strategies to monitor the fate of nanostructured drugs in cell models

Maria Montes Bayón, Mario Corte, Roberto Álvarez-Fernández, Daniel Turiel, Jenifer Garcia, Jörg Bettmer, Elisa Blanco

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Biomaterials with nano-scale organizations have been used as controlled release reservoirs for drug delivery and artificial matrices for tissue engineering. Drug-delivery systems can be synthesized with controlled composition, shape, size and morphology and these nanocarriers can be successfully used as platforms for drug delivery to sensitize cells to chemotherapy among others.[1] In fact, the use of nanotechnology to develop nanodelivery systems has allowed researchers to overcome limitations of antineoplastic drugs by increasing the solubility of the drug and decreasing the toxicity to healthy tissues. But not only in the case of chemotherapy, also for treatment of iron deficiency, the use of 5-10 nm hydro-disperse particles of iron oxo-hydroxide that have been modified synthetically with the addition of tartaric and adipic acids have proved to delivers safe iron that is well absorbed and utilized in humans mimicking the well-absorbed ferritin core.

However, the use of such nanocarriers in clinical studies is going to be conditioned by the development of adequate analytical tools that permit the monitoring of the fate of such formulations in complex biological matrices. In this regard, this presentation will illustrate the design and evaluation of new platforms to permit the sensitive monitoring of iron and platinum drugs in cell models using ICP-MS based strategies. The suitability of the proposed strategies will be applied to the evaluation of nanostructured iron treatments used to overcome Fe deficiency and in the study of cisplatin encapsulation in ferritin nanocages.

1.David R. Khan. The Use of Nanocarriers for Drug Delivery in Cancer Therapy. J Cancer Sci Ther. 2(3): 058-062 (2010).

MT-OL: METALLOMICS - GENERAL SESSION

Time: Wednesday, 22/Feb/2017: 4:10pm - 5:50pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Stephan Hann

Session Chair: Luis Gálvez

4:10pm - 4:20pm

MT-OL: 1

Topics: Elemental analysis, Nanomaterials

Keywords: Single cell analysis, ICP-MS, LA-ICP-MS

Single Cell Analysis Based on Inductively Coupled Plasma Mass Spectrometry

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Cell was the basic unit of all known living organisms which was critical for exploring the law of life and indicating the mechanism of diseases. Previous studies generally focused on the cell colony and the obtained information was commonly the average of many cell individuals. However, each cell has a different behavior. Single cell analysis can accurately obtain valuable information of each cell in the microenvironment and thus there is an urgent need for single cell analysis. A new method based on inductively coupled plasma mass spectrometry (ICP-MS) has emerged for single cell analysis.

In the plasma, all chemical bonds in the sample are easily broken and analyte isotopes are effectively ionized into positive ions. Under the time resolved mode, the frequency and intensity of signals from ICP-MS is directly related to the number concentration of cells and elemental mass per cell. The developed single cell ICP-MS (SC-ICP-MS) was used to determine intracellular $Gd@C_{82}(OH)_{22}$ and cisplatin after treatment of Hela and 16HBE cells at a single-cell level. Cisplatin is a commonly used chemotherapeutic drug, whereas $Gd@C_{82}(OH)_{22}$ is a new nanomaterial anti-tumor agent. The quantitative measurement of the cellular uptake of drugs is of great importance, especially down to single cells, may provide the most important information for personalized therapies. The cell digestion method validated the accuracy of the SC-ICP-MS. The concentrations of $Gd@C_{82}(OH)_{22}$ and cisplatin in cells at different exposure time and doses were studied. Data show that $Gd@C_{82}(OH)_{22}$ has higher bioavailability and lower toxicity than cisplatin in vitro, and thus make it possible to inhibit tumor at a low dose. The capability of ICP-MS for single cell analysis was thus demonstrated here. The SC-ICP-MS is promising complement to available methods for single cell analysis and is hopeful to be further applied to biomedical research.

Laser ablation ICP-MS (LA-ICP-MS) is a technique used for the in situ analysis of trace elements in solid samples. Unlike solution-based techniques, LA-ICP-MS enables in situ analysis of microscopic targets, offering new opportunities for single cell analysis. Here, we demonstrate a new method, based on LA-ICP-MS, which can quantify in situ gold nanoparticles (Au NPs) in single cells. Dried residues of picoliter droplets ejected by a commercial inkjet printer were used to simulate matrix-matched calibration standards. The gold mass in single cells exposed to 100 nM NIST Au NPs for 4 h showed a log-normal distribution, ranging from 1.7 to 72 fg Au per cell. The average result from 70 single cells (15±13 fg Au per cell) was in good agreement with the result from an aqua regia digest solution of 1.2×10^6 cells (18±1 fg Au per cell). The limit of quantification was 1.7 fg Au. LA-ICP-MS is a sensitive and versatile technique for single cell analysis and will offer great benefit to the study of biological responses to metal drugs or NPs at the single cell level.

4:20pm - 4:30pm

MT-OL: 2

Topics: Coupling techniques (chromatography, FFF, ETV, others), Metallomics
Keywords: LC-ICP-MS, metal tag reagent, delivatization, amino acid, organic acid

The highly sensitive analytical method of the metabolite: Development of the metal tag reagents for the low molecular weight hydrophilic compound.

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The organic compounds are usually unable to be detected with inorganic analytical instrument, ex. ICP-MS and ICP-AES. Then, the new analytical method using the metal tag has been development to determine the protein and the peptide. The metal tag is the functional group for ICP-MS detection. It contains a metal atom, a metal colloid, a nanoparticle or other metal forms, and it is joined to the analyte by the metal tag reagent. The famous metal tag reagent for protein is DOTA (1, 4, 7, 10 - tetraazacyclododecane *N, N‘, N”, N’”* - tetraacetic acid). It is suitable to analyze with LC-ICP-MS. It is expected that the analytical method with metal tag will be widely used to detect the ultratrace organic compounds.

On the other hand, it has not been reported the metal tag reagent for the analysis of the low molecular weight compound like metabolites; amino acid and organic acid. Their properties are quite different from that of protein. The most of their compounds have the highly hydrophilicity and the similar chemical structure. They are need the high separability to analyze with HPLC. Therefore, the reverse phase HPLC is quite used. Then, the metal tag for the metabolites has a different nature from those of the protein. It certainly has not just role of the detective target, but adequate hydrophobicity to keep inside the reverse phase column.

We have developed and examined the various compounds to use for the metal tag for the hydrophilic metabolites. We will report the result of our study.

4:30pm - 4:40pm

MT-OL: 3

Topics: Application of speciation analysis

Keywords: GC-ICP-MS, IC-ICP-MS, speciation, organo phosphates, lithium ion battery electrolytes

Application of 2D-IC-ICP-MS and GC-SF-ICP-MS for the Speciation of Organophosphates in Lithium Ion Battery Electrolytes

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Lithium-ion batteries (LIBs) are the most promising technology for electric and hybrid electric vehicles. Unfortunately, the lifetime of LIBs is limited due to electrochemical, thermal and calendric aging. Currently applied electrolytes for LIBs usually consist of $LiPF_6$ as conducting salt dissolved in a mixture of different linear and cyclic organic carbonates. Despite the chemical and thermal instability in organic carbonates towards the P-F bond, $LiPF_6$ is the most commercial applied conducting salt today. However, due to its instabilities, hexafluorophosphate undergoes a complex decomposition process. As a consequence, numerous decomposition products are formed and are an ongoing subject of investigations with different methods. The variety of decomposition products ranges from HF, inorganic and organic phosphates (OPs), dicarboxylates, diols and alkyl fluorides.

Since several of the identified decomposition products contain a structural resemblance to certain nerve agents, the toxicity of Organophosphates is because of their reaction with the enzyme acetylcholinesterase (AChE). AChE hydrolyses acetylcholine, a neurotransmitter regarding muscles and organs. During the reaction, a covalent bond between the organophosphate and the AChE is formed and subsequently stopping the enzyme from functioning. Therefore, investigation of LIB electrolyte decomposition products in terms of qualitative and quantitative information is not only important for the electrochemical life time, but as well for potentially toxicological aspects. So far, only few information about the toxicity and even fewer about quantitative data are available in literature.

In this work, we present our approach to obtain structural and quantitative information about the decomposition products, especially the potential toxic compounds, by combination of inductively coupled plasma mass spectrometry with different chromatographic methods like ion chromatography or gas chromatography.

4:40pm - 4:50pm

MT-OL: 4

Topics: Application of speciation analysis, Metallomics
Keywords: ICP-MS/MS, chromium, Cr(VI), blood, erythrocytes

Application of ICP-MS/MS for the clinical determination of chromium (VI) in human erythrocytes and chromium in blood, plasma and urine

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The determination of chromium in human biological materials such as whole blood, plasma, erythrocytes and urine has clinical relevance in occupational and environmental health. For chromium blood determinations the two major analytical problems are possible contaminations in the pre-analytical phase and strong spectral interferences from polyatomic ions in ICP-MS (e. g., $^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$, $^{34}S^{18}O$, etc.). Digestion of the samples can reduce some spectral interferences but enhances the risk of new contaminations in the sample preparation step. For this reason we prefer a dilution of blood samples with a 0.5% (V/V) ammonia solution prior to analysis and to overcome spectral interferences we apply ICP-MS/MS with ammonia as reaction gas (reaction of ^{52}Cr with NH_3 to $^{86}Cr(NH_3)_2$ ions).

We also discuss the clinical significance of the different biological materials and strategies to minimize contaminations during the sample collection phase. The analysis of isolated erythrocytes from the blood reflects an exposition to carcinogenic Cr(VI), because the cell membranes are impermeable for Cr(III) and only Cr(VI) is transported into the erythrocytes. The Cr(VI) concentrations in erythrocytes and the distribution of the Cr species in the different human biological fluids are described for selected clinical case studies, e.g., the occupational exposure to welders, wear of implanted hip prostheses containing chromium or in a severe chromium arsenate intoxication.

4:50pm - 5:00pm

MT-OL: 5

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis, Metallomics
Keywords: Capillary electrophoresis, ICP-MS, hyphenation, interface, cisplatin

Towards routine capillary electrophoresis hyphenation to ICP-MS

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Capillary electrophoresis (CE) is an ideal technique for characterizing metal-based anticancer complexes' stability and binding affinity with potential biological targets [1]. These preliminary studies contribute to optimal drug candidates being invested into clinical trials and continuing on to subsequent commercialization. Hyphenation of CE to an inductively coupled plasma–mass spectrometer (ICP-MS) means even higher specificity and sensitivity can be achieved. CE–ICP-MS hyphenation can be very challenging as there are various technical aspects that must be considered to maintain separation efficiency [2]. A means of hyphenation of CE to ICP-MS will be presented that is considerably simpler than the two currently commercially available interfaces, the CEI-100 and the Mira Mist CE interface, without sacrificing gelectropherogram quality or sensitivity [3]. We present key points in the development and optimization of the interface including construction methods and materials, sheath liquid composition and key ICP-MS parameters such as capillary position, sheath liquid flow rate and carrier gas flow rate. The interface is compared with alternative methods of hyphenation including the commercially available CEI-100 interface from CETAC [4].
Considerable improvement of the peak shape and the analytical features such as peak area, and migration time repeatability is shown for a cisplatin-based test system. Finally, a study of the interaction of cisplatin with various biological targets including the proteins human serum albumin, transferrin and ubiquitin, as well as the nucleotide guanosine 5'-monophosphate carried out with this CE-ICP-MS interface is presented.
Our new method of hyphenation is inexpensive, considerably easier to assemble and operate, and more robust than systems currently on the market. It has significant potential to make CE–ICP-MS a more accessible scientific technique resulting in more widespread use.

References:
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[2] Michalke, B., Electrophoresis 2005, 26, 1584-1597.
[3] Møller, C., Sturup, S., Hansen, H., Gammelgaard, B., J. Anal. At. Spectrom. 2009, 24, 1208-1212.
[4] Schaumlöffel, D., Prange, A., Fresenius J. Anal. Chem. 1999, 364, 452-456.

5:00pm - 5:10pm

MT-OL: 6

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Nanomaterials
Keywords: elemental imaging, fingerprint, nanoparticles

Elemental analysis and imaging of human fingerprints: a new technique for forensic sciences

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Human fingerprints are unique and durable over the life of an individual. The fingerprints are suitable for human identity and thus usually are employed by authorities to identify criminals and victims. Traditional methods are mainly focused on rendering fingerprints visible. Other emerging methods aim at providing additional chemical information (usually organic molecules) from fingerprints, making it possible to characterize fingerprint owners. For example, if metabolites of a medicine are found in a fingerprint, it is able to deduce that the fingerprint owner probably took the medicine before.

Here we utilized atomic spectrometric methods including synchrotron radiation X-ray fluorescent (SRXRF), X-ray fluorescent (XRF), and laser induced breakdown spectroscopy (LIBS) to analyze and image trace elements in fingerprints. Besides natural existing elements, such as sodium, calcium, potassium, etc., specific elements in fingerprints from daily commodity containing metal nanomaterials could be determined and imaged simultaneously by the above methods. The determination and imaging of elements fingerprints is beneficial to identify fingerprint owners, opening a new door for forensic study.

5:10pm - 5:20pm

MT-OL: 7

Topics: Sample introduction and sample preparation, Metallomics

Keywords: single cell ICP-MS

Advances in single-cell ICP-MS for determining elemental distributions in cell populations

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PURPOSE: The determination of metals, metalloids and other elements in individual cells is of significant interest in view of cell population heterogeneity. Knowledge of elemental distributions in cell populations, as opposed to average concentration values, is therefore vital for improved insight into their cellular uptake and biochemistry. However, little progress has so far been made in this particular area of analysis, mainly because of low sensitivity, limited data processing capabilities and inability to fully interpret the obtained data and relate it to biological processes.

In this study we present our efforts to develop, optimize and validate single cell (SC) ICP-MS methods for the determination of metal uptake by *Chlamydomonas rheinhartii* cells in metal incubation experiments, as well as for determining naturally occurring elements. For this purpose the mass balance of metals and comparisons with average metal concentrations determined from digested cell samples were made.

METHODS: SC ICP-MS methods were developed using a fast scanning quadrupole ICP-MS system (NexION 300xx, PE) with capabilities for fast data acquisition. Here we evaluated the quality of data obtained using detector dwell times ranging from 50 µs to 10 ms. In addition, features of Syngistix™ Nano (PE) software were evaluated for SC analysis.

RESULTS: The effect of various experimental parameters on SC ICP-MS analysis were investigated. These parameters include detector dwell times (ranging from 50 µs to 10 ms), injector torch i.d., plasma gas flows, spray chamber configurations, ICP-MS universal cell conditions, sample introduction flows and cell number concentrations. The potential of using this approach to investigate the occurrence of cellular aggregation is also studied. Examples will be provided for the uptake of Cd, Pb, Cr and Ni, in addition to naturally occurring elements such as Mg, Cu, P, K, Na, Ca, as well as several others.

CONCLUSIONS: Even though SC ICP-MS is still in its infancy as a bioanalytical technique, it does demonstrate potential for metal determination in individual cells as shown in this and other recent studies. New improvements in sample introduction configurations, mass analyzers and instrument electronics and software are expected to further improve the state of this new technique.

5:20pm - 5:30pm

MT-OL: 8

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: imaging, tumor tissue, cytostatic, Pt, LA-ICP-MS

Pt-based cytostatics: Where are they accumulated?

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One of the main group of drugs that inhibit cell growth are Pt-based cytostatics – cis-, carbo- and oxali-Pt. They are simple molecules with incorporated Pt and their treatment differs. Our hypothesis is that this various treatment should results in a different distribution of Pt in melanoma tissue.

For this purpose, we examined 4 different groups of mice with prostatic melanoma. Three of them were treated by cis-, carbo-, and oxali-Pt, respectively and fourth was not treated any drug. The melanomas were resected from each mice and were cut into thin section form. Distribution of Pt, Cu, Zn was studied using LA-ICP-MS method. The distinct differences are observable not only in the distribution of Pt but also in the amount of Pt that got into tumor tissue. Moreover, distribution of Cu and Zn varies, as well depending on applied cytostatic. The obtained results could be useful in explanation of cytostatics treatment and their mechanism.

Authors thank to the project CEITEC 2020 (LQ1601) of the Ministry of Education, Youth and Sports of the Czech Republic.

5:30pm - 5:40pm

MT-OL: 9

Topics: Application of speciation analysis

Keywords: arsenic, speciation, LC-ICP-MS, rice

A novel take on ion interaction chromatography for fast and sensitive arsenic speciation analysis in rice using LC-ICP-MS

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The need for measuring inorganic arsenic (as opposed to total arsenic, which includes organo-arsenic species) is increasing in the food industry. In particular, rice and rice derived products have been the focus of recent legislation on arsenic limits. This generates a large demand for speciation testing and a need for methods that are fast, sensitive, and robust.

In order to separate the arsenic species prevalent in rice, the default LC-ICP-MS implementation utilizes anion exchange chromatography or alternatively, ion interaction chromatography with an anion pairing reagent. Both of these methods employ circumneutral or alkaline conditions to ionize most of the target analytes with run times typically ranging from 9 – 15 min, and As5 eluting last, which is unfavorable for sensitivity purposes. Here we report application data for arsenic speciation using ion interaction chromatography with a cation pairing reagent using a mobile phase at acidic conditions. The limited role of attractive forces in this approach results in reversed elution order of the species and very short run times of 3 min whilst maintaining baseline resolution of the peaks.

We will present details of the method development, and data on the application of the optimized method to rice samples for the baby food market and rice derived products. Samples were extracted with 0.28 M HNO_3 for 90 min on a hotblock employing an extraction scheme which had previously been validated to maintain species integrity. As3, As5, MMA (monomethylarsonic acid) and DMA (dimethylarsinic acid) were quantitated by external calibration using a PerkinElmer Altus HPLC and NexION 350 ICP-MS. Inorganic arsenic was determined as the sum of As3 and As5 and ranged from 18 to 130 ppb, bracketing the 100 ppb regulatory limit for baby food rice. Spike recoveries for all samples and all analytes averaged 104 -106%. A certified reference material, NIST 1569b rice flour, was analyzed in duplicate with recoveries ranging between 97-99% for inorganic arsenic, MMA and DMA. The detection limit for As3 and As5 of 2.5 ppb on a solids basis was sufficient to analyze the lowest encountered concentrations and can be further improved by increasing the injection volume.

In summary, an attractive alternative to the mainstream analytical approach for arsenic speciation is presented. The method is characterized by a much faster run time, is sensitive for early eluting inorganic arsenic species and sufficiently robust to assure accurate analysis of rice and rice derived products targeted by recent regulations.

5:40pm - 5:50pm

MT-OL: 10

Topics: Metallomics

Keywords: metallophores, metallomics, metal complexes

DEVELOPMENT OF ANALYTICAL APPROACHES TO UNRAVEL METAL COMPLEXES AND MORE SPECIFICALLY METALLOPHORES IMPLICATED IN METAL HOMEOSTASIS IN CELLS

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Purpose

Metal ions are necessary for numerous biological processes and living organisms developed multiple mechanisms to insure their uptake and homeostasis. They are often facing a significant limitation in the bioavailability in their close environment for most of the essential transition metals (Fe, Zn, Cu, Mn, Co, Ni, Mo…) due to their low concentrations, their low solubility, excess of competing metal ions and/or competitions for metal uptake with other organisms. To overcome this issue, they produce molecules that will form metal complexes to improve metal handling. To determine the actual nature of the implicated metal complexes and metallophores is therefore of utmost interest.

Methods

Appropriate sample preparation was followed by the analysis by coupling of hydrophilic interaction chromatography (HILIC) or size exclusion chromatography (SEC) with inductively coupled plasma mass spectrometry (ICP MS) and high resolution electrospray mass spectrometry (HR ESI MS). It allowed the detection and quantification of metal complexes in various type of samples (plants, bacteria, pathogenic bacteria…).

Results

Several metal complexes (more than fifty) in plant saps (Flis et al. 2016 New Phytologist) or novel metallophores (such as nicotianamine-like compounds) in non-pathogenic or pathogenic bacteria (Ghssein et al. 2016, Science) could be identified.

Conclusion

This work allowed to improve the comprehension of metal homeostasis in several organisms.

LA-PL: LASER-ASSISTED ANALYSIS / GLOW DISCHARGE - PLENARY LECTURE 1

Time: Thursday, 23/Feb/2017: 8:30am - 9:00am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Cornel Venzago

Session Chair: Lisa Fischer

8:30am - 9:00am

LA-PL: 1

Topics: Sample introduction and sample preparation, Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Laser Ablation, Imaging, LIBS, ICP-MS

Laser Ablation Influence on Elemental and Isotopic Analysis

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Over the past fifty-plus years, laser ablation (LA) has developed into a mainstay technology for direct solid sampling in analytical chemistry. The driving forces include rapid analysis, no acid digestion, spatial resolution, and more. These attractive features have helped propel LA over other technologies for imaging, escpeially because laser abaltion does not require vacuum and can be applied to any sample matrix.

Laser ablation is the sampling process not the analysis; a short-pulsed laser beam removes mass (sampling) for subsequent analyis. The laser sampling process can be optimized separately from the detection modality. The ablated mass is initially forms a luminous optical plasmas at the sample suface that is spectroscopically measured (LIBS – Laser Induced Breakdown Spectroscopy) for elemental content. As the plasma cools, the mass condenses to a fine aerosol which can be transported to an Inductively Coupled Plasma (ICP). Laser fluence, wavelength and pulse duration influence ablation behavior and therefore analytical performance. Optimization of LIBS and ICP detection depends on the measurement requirements.

The ICP with mass spectrometry (MS) is ideal for trace analysis of isotopes, especially for the heavier elements. LIBS is ideal for analyzing major concentrations and light elements, including O, N, H and halogens. LIBS monitored simultaneously with ICP-MS detection provides complementary elemental and isotopic analysis of the sample, for every laser pulse and at every spatial location.

Our new technology LAMIS (Laser Ablation Molecular Isotopic Spectroscopy) measures isotopes in laser plasmas at atmospheric pressure from molecular emission band spectra in addition to atomic and ionic line spectra. To date, we have demonstrated LAMIS by measuring B, C, H, D, Sr and other isotopes. For some isotopes, we have achieved < 0.1% precision with sensitivity in the ppm range.

For imaging, laser ablation with simultaneous ICP-MS, LIBS and LAMIS offers the ability to measure every element/isotope with fine spatial resolution. The talk will cover the capabilities of laser ablation sampling with LIBS, LAMIS and ICP-MS with reference to other technologies like Glow-Discharge Mass Spectrometry (GDMS) for chemical imaging and analysis. In addition, because LIBS and LAMIS are all-optical technologies, they are suited for spatial analysis at remote standoff distances. Conventional focusing of laser beams for distance is reliant on the size of the aperture. However, with femtosecond laser pulses, non-linear absorption processes allow the beam to form guided filaments, distance mainly dependent on the laser energy and pulse duration. These filaments can be used for ablation of a sample at a distance. By coupling femtosecond –filaments with LAMIS (F^2-LAMIS), we have measured elemental and isotope ratios of samples at distances up to 70 meters (distance limited at this time to open-path space in our laboratory).

LA-IL 1: LASER-ASSISTED ANALYSIS / GLOW DISCHARGE - INVITED LECTURES 1

Time: Thursday, 23/Feb/2017: 9:00am - 9:20am
Location: ARLBERG-well.com NORTH HALL
Session Chair: Cornel Venzago
Session Chair: Lisa Fischer

9:00am - 9:20am

LA-IL 1: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Laser Ablation, Elemental Imaging, Time-of-Flight Mass Spectrometry

High-Resolution LA-ICP-TOFMS Imaging: From Instrumentation to Interpretation

Alexander Gundlach-Graham[1], Gunnar Schwarz[1], Marcel Burger[1], Paolo S. Garofalo[2], Bodo Hattendorf[1], Detlef Günther[1]
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Elemental imaging by LA-ICPMS continues to move toward higher lateral resolution and faster image-acquisition speed. These advances have been made possible through technology developments in low-dispersion LA cells and ICPMS instrumentation. In our lab, elemental imaging with LA-ICP-TOFMS is now routinely achieved with laser-spot sizes at or below 5 µm and pixel-generation rates up to 100 pixels/s. At a spot size of 5 µm, single-laser-shot detection limits are typically in the low µg g^{-1} range for the rare-earth elements and heavier; most lighter elements have detection limits in the 10s–100s of µg g^{-1}. High-speed, laser-shot-resolved multi-elemental images of up to 1 MP (megapixel) and beyond can now be obtained in an afternoon; this speed-of-analysis opens the door to imaging large sample areas at high resolution in order to accurately characterize micro-to-macro features across a sample surface. While the instrumentation to obtain high-pixel-density, multi-elemental LA-ICPMS images can be considered—to some extent—developed, analysis and interpretation of these images remains largely unexplored.

In this presentation, we highlight the current state of our LA-ICP-TOFMS imaging method. We describe several LA-ICP-TOFMS imaging case studies to illustrate the importance of data handling and analysis. Specific emphasis will be placed on strategies for the quantification of elements across multiple domains (i.e. matrices) in a sample surface. We explore the relationships between laser spot size, lateral resolution, and quality of elemental quantification within features of an elemental image. Ultimately, the relevance of high-resolution LA-ICP-TOFMS depends on the generation of accurate images and the development of methods to extract element or isotope abundance information to support image interpretation. Here, we aim to discuss current strategies, shortcomings, and future directions of high-resolution LA-ICPMS image generation and interpretation.

LA-OL 1: LASER-ASSISTED ANALYSIS / GLOW DISCHARGE - GENERAL SESSION 1

Time: Thursday, 23/Feb/2017: 9:20am - 10:10am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Cornel Venzago

Session Chair: Lisa Fischer

9:20am - 9:30am

LA-OL 1: 1

Topics: Glow discharge mass spectormetry

Keywords: Solar cells, Depth profile characterisation, Glow discharge sources, Pulsed mode, Time of flight mass spectrometry

Characterisation of new thin film solar cell photovoltaic devices using the state-of-the-art pulsed radiofrequency glow discharge time of flight mass spectrometry

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Photovoltaic solar cell performance strongly depends on parameters such as layer thicknesses, dopant element concentrations, presence of impurities and diffusion processes. To understand these internal material performances, studies of their optical and electrical properties through inferred and restrictive measurements are traditionally undertaken. However, alternative strategies are still sought to establish the correct chemical characterisation and relate this to the photovoltaic device efficiency.

Fast and reliable solid-state spectrometric techniques are required for depth profiling analysis of solar cells. Glow discharge (GD) sources coupled to optical emission and mass spectrometry provide a powerful tool for depth profiling analysis of conducting and non-conducting materials with high depth resolution. Additionally, suitable combination of pulsed GDs (PGDs) with a time of flight mass spectrometer (ToFMS) enables time-gated detection of ions along the GD pulse period and, thus, selection of the integration time window that provides the highest analyte signal with minimum spectral interference.

- **Methods**

A thorough study of PGD-ToFMS capabilities for the characterisation of different types of next generation thin film solar cells (TFSCs) will be shown. In general, TFSCs have lower production costs compared totraditional crystalline silicon solar cells, requiring nontoxic and abundant raw materials. However, the main disadvantage of this type of devices is the low efficiency. Thus, PGD-ToFMS was evaluated for a complete depth characterisation of different type of photovoltaic devices, including solar cells based on hydrogenated amorphous silicon (a-Si:H), tandem-junctions solar cells, perovskite solar cells and SnS based solar cells.

- **Results**

Fast and sensitive qualitative and quantitative (a-Si:H solar cells) determination of matrix and dopant elements in different types of solar cells have been performed by PGD-ToFMS. Elemental diffusion processes between the coating layers were identified for a-Si:H and tandem-junctions solar cells. Also, it was found that the thickness of the front contact aluminium-doped ZnO layer has a direct influence on the distribution of dopant elements in the a-Si:H layer. Concerning perovskite and tandem-junction solar cells, different synthesis processes were evaluated by PGD-ToFMS and a different distribution of dopant elements was found depending on the sample preparation step.

- **Conclusions**

Experimental results showed that GD-ToFMS, operated in the radiofrequency pulsed mode, is a fast and reliable analytical tool to simultaneously determine chemical composition and thickness of the strategic layered structures of solar cells. Thus, the findings of this work can help to investigate in more detail the synthesis process of the samples and so the further practical development of these photovoltaic cells.

9:30am - 9:40am

LA-OL 1: 2

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LIBS, Shale and Core Samples, IR Microscopy, Hydrocarbon

Laser Induced Breakdown Spectroscopy for High Resolution Mapping of Core Samples

C. Derrick Quarles Jr.[1], Francisco Lopez-Linares[2], Toni Miao[2], Laura Poirier[2], Jhanis J. Gonzalez[1,3]

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Oil and Gas companies rely on core geologic sampling and the analyses of these samples can help to predict and understand specific oil and gas reserves. Rock samples, which are the result of core sampling, reveal many details regarding the history and formation of wells and reserves. These core samples are an essential component to assess the fundamental geological properties of the hydrocarbon reserves as they are the only direct evidence available from beneath the earth. They provide the upstream operators with an opportunity to view the characteristics of the reservoir that has been encountered. These samples contain information in terms of hydrocarbon nature, porosity, grain size, and mineralogy which are all important factors that can influence decisions about drilling locations.

To access the hydrocarbon component from the mineral, it needs to be extracted from the solid matrix by various types of standard protocols, which can be lengthy, and then dried before analysis can occur. These dried samples are then characterized using many different surface techniques. The possibility to obtain this information with minimum to no sample preparation is investigated.

Laser Induced Breakdown Spectroscopy (LIBS) and Infrared (IR) Microscopy will be used to evaluate two core samples from North America. LIBS is a fast analytical technique that can provide elemental information both laterally and in-depth of a given sample. While IR Microscopy is a relatively easy technique that provides information about the functional group's existing on the hydrocarbon. The mineral composition and the hydrocarbon structural characteristics obtained from IR microscopy will be used with data collected from LIBS, to produce high-resolution images that all information, without using any sample preparation method.

9:40am - 9:50am

LA-OL 1: 3

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Environmental sciences
Keywords: LA-ICP-MS, quantitative analysis, ultrafine particles

LA-ICP-MS analysis of size segregated ultrafine airborne particulates

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For assessment of adverse health effects of toxic metals present in airborne particulate matter (APM) usually the size fractions below 10 µm and 2.5 µm aerodynamic diameter are considered (PM10 and PM2.5, respectively). However, for ultrafine particles (UFP) an enhanced toxicity is expected since the respiratory deposition is distinctly increased when compared to larger particles, which are separated to a bigger part in the in the pharyngeal and tracheal region. In contrast to PM2.5 and PM10, only few studies report metal contents in the size fraction below 1 µm; problems in analysis due to restricted sample amounts and the complex composition of APM being the main limitations.

This contribution presents an innovative approach for quantitative LA-ICP-MS analysis of size segregated APM samples. A 13-stage low pressure impactor (DLPI) was used for the collection of size-segregated UFP at an urban background site in Como (Italy). Particles ranging from 0.03 to 10 µm were deposited on high-purity polycarbonate as sampling substrate. For analysis, a representative number of sample spots from each impactor stage was analyzed using line scan patterns, which enabled quantitative ablation of the investigated sample spots with sizes ranging from less than 100 to more than 1 mm diameter. Quantification of derived transient signals was accomplished using dried-droplets of aqueous standard solutions; analysis has been performed using the LA-ICP-MS procedure developed for measurement of UFP samples. For method validation, one set of impactor samples was additionally measured using conventional ICP-MS analysis after complete sample mineralization with a mixture of different acids. Accuracy of this standard approach was demonstrated by analysis of NIST SRM 1648a (urban particulate matter). Comparison of ICP-MS results with the data acquired using the proposed LA-ICP-MS procedure revealed an excellent agreement. Finally, the procedure was applied for analysis of an extended set of UFP samples providing information about the seasonal variation of selected trace elements.

9:50am - 10:00am

LA-OL 1: 4

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Coupling techniques (chromatography, FFF, ETV, others)

Keywords: Electrothermal Vaporization, femtosecond, nanosecond, Laser Ablation, Metals, Signal Suppression

A comparison of signal suppression rates and particle size distributions for ns- and fs-LA-ETV-ICPMS for pure and alloyed metallic standards

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It was shown for a large variety of samples [1], that the thermal treatment of laser-generated aerosols in an Electrothermal Vaporization (ETV) unit triggers changes in its chemical composition. For those studies, aerosols generated by ns-laser ablation (ns-LA), were guided from the ablation chamber through the heated graphite furnace of an HGA-600MS ETV unit. Ion signals were recorded by ICPMS. Different either element-specific or unspecific signal decrease regimes were observed, caused by multiple underlying mechanisms. To investigate those further, in this study, the signal suppression for aerosols generated by ns- or fs-LA were compared for pure Cu, Zn, Ta and brass (62.9% Cu, 30.0% Zn). The stoichiometry of fs-LA-generated aerosols represents the one of the bulk more accurately and the concentration of large particles within the aerosol is lower compared to ns-LA, especially for metallic samples. [2, 3] Therefore, differences in signal behavior as function of the graphite furnace temperature are expected for the two LA-systems. Either a fs-laser (Excite Pharos, 206 nm, Teledyne Cetac) or a ns-laser (GeoLas-C, 193 nm, Coherent) was coupled to the ETV unit (HGA-600, Perkin Elmer) for aerosol heating and a Q-ICPMS (Elan 6100 DRC^{plus}) for analysis of the ion signals. An element-specific suppression was observed, depending on the vaporization temperature of the element. Therefore, not only the onset of signal decrease was individual for every ion signal, but also the extent of suppression. While for Ta, only a slight suppression was observed for both LA-systems, starting at 1’900° C, the vaporization of Cu and Zn started at lower temperatures. For Zn, the signal suppression started at 500° C, for Cu at 1’500° C, both for the pure metals and brass. For fs-LA, the suppression was up to one order of magnitude stronger compared to ns-LA, which is assumed to be a result of a more efficient vaporization process due to the smaller mean particle size within the aerosol.

10:00am - 10:10am

LA-OL 1: 5

Topics: Elemental analysis, Glow discharge mass spectormetry

Keywords: Sector Field-Glow Discharge-Mass Spectrometry, Lithium Ion Battery

Investigation of Lithium Ion Battery Electrodes by means of Sector Field-Glow Discharge-Mass Spectrometry (SF-GD-MS)

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The state-of-the-art Lithium Ion Battery (LIB) negative electrodes consist of graphite with a decent capacity 372 mAh g^{-1} and lithium transition metal oxides ($LiMO_2$) as positive electrodes supplying capacities of roughly 150 mAh g^{-1} (*M* = Mn, Co, Ni). Popular positive electrodes are ternary mixtures of nickel, cobalt and manganese with different benefits and drawbacks, like high thermal stability and higher capacities in the charged state as well as less toxicity.[1] On the other hand, these materials suffer from fading capacities during continuous cycling which cause is not fully understood.

One postulated cause is assigned to the passivation layer on the negative electrode which is formed during the first cycle due to the high reductive potentials. This passivation layer is called Solid Electrolyte Interphase (SEI) and grows with ongoing cycling and consumes active lithium which is resulting in capacity losses. Furthermore, the dissolution of transition metals - originating from the positive electrode – were claimed to have an influence on the SEI as it affects the surface of it.[2] The common method to examine passivation layers in battery research is the use of X-ray Photoelectron Spectroscopy (XPS) which suffers from poor depth resolution as well as long measurement times due to small sample spots.[3]

In order to examine the effect of SEI growth and transition metal deposition on negative electrodes, the Sector Field-Glow Discharge-Mass Spectrometry is an outstanding tool for the depth resolved analysis of these layers as slow sputter rates can be achieved. Furthermore, the possibility to measure elements like fluorine or phosphorus gives further clues on the structure and composition on the SEI.

In this work, the SF-GD-MS is used to quantify the depth resolved content of lithium in cycled electrodes as well as the content of transition metals on graphitic negative electrodes. Furthermore, fluorine and phosphorus signals were affiliated in order to observe SEI changes in detail. Self-prepared matrix matched standards with elevated contents of lithium, nickel, cobalt and manganese in order to perform external calibration were measured. The bulk concentrations of the element spiked electrodes are validated *via* ICPOES.

The obtained results for the transition metal dissolution[1] and the bulk lithium[2] content are compared to established methods using Total Reflection X-Ray Fluorescence (TXRF)[1] and ICPOES[2].[4]

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[2] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.-C. Möller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, *J. Power Sources*, 147 (2005) 269-281.

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LA-IL 2: LASER-ASSISTED ANALYSIS / GLOW DISCHARGE - INVITED LECTURES 2

Time: Thursday, 23/Feb/2017: 10:50am - 11:30am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Cornel Venzago

Session Chair: Lisa Fischer

10:50am - 11:10am

LA-IL 2: 1

Topics: Glow discharge mass spectormetry

Keywords: Glow Discharge, Mass Spectrometry, Materials, depth profile

Trends and challenges in Glow Discharge Mass Spectrometry for Direct Analysis of Innovative Materials.

Jorge Pisonero, Jonatan Fandino, Alfredo Sanz-Medel, Nerea Bordel

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Manufacturing industry requires the development and characterization of challenging materials (e.g. photovoltaic cells, production of high wear-resistant coatings, hard-disks, Ni and Co super-alloys, etc.). In this context, the ability to accurately analyse and characterise bulk and layered materials is essential to the development of new products and processes.

Atomic spectrometry techniques have long been used for direct elemental chemical characterization. For instance, Secondary Ion Mass Spectrometry, Auger Electron Spectroscopy, or X-Ray Photoelectron Spectroscopy, are techniques that provide very valuable information about the chemical composition of the surfaces/coatings. However they also have some major drawbacks, such as high operating costs, complex sample pre-treatment and handling, low sample throughput and/or severe matrix effects that result in difficult quantification procedures. Other techniques, such as those base on laser ablation or laser induced plasma (e.g. LA-ICP-MS, LIBS, LAMS), provide high spatial resolution and high sensitivity but their depth resolution capabilities are restricted to a few tens or hundreds of nanometers.

In order to overcome some of these drawbacks Glow Discharge Mass Spectroscopy (e.g. GD-TOFMS and GD-SFMS) is proposed as a complementary methodology that provides an ideal solution for fast and accurate bulk and layer analyses [1,2]. Here, we evaluate and critically discuss the advantages and limitations of this technique, the recent progresses, and the new applications.

[1] C. Venzago, J. Pisonero; “Glow discharge mass spectrometry", Sector Field Mass Spectrometry for Elemental and Isotopic Analysis (editors T. Prohaska, J. Irrgeher, A. Zitek and N. Jakubowski), Series of New Developments in Mass Spectrometry, Volume 2015-January, Issue 3, 2015, Pages 319-380; DOI: 10.1039/9781849735407; ISBN: 978-1-84973-392-2.

[2] J. Pisonero, N. Bordel, C. Gonzalez de Vega, B. Fernández, R. Pereiro, A. Sanz-Medel, “Critical evaluation of the potential of radiofrequency pulsed glow discharge time of flight mass spectrometry for depth profile analysis of innovative materials”, Analytical and Bioanalytical Chemistry, 2013, 405(17), 5655-5662.DOI 10.1007/s00216-013-6914-1.

11:10am - 11:30am

LA-IL 2: 2

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: Laser Ablation Mass Spectrometry, CD-nozzle, Ion Funnel

Taming Laser-Generated Ions for Their Use in Mass Spectrometry

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Ions generated in a high-energy laser plasma in vacuum were already studied in the early 1960s [1] for fundamental and soon also analytical purposes [2]. However, the broad angular and energy distribution of these ions ever made it difficult to collect and transport them into a mass spectrometer with highest efficiency. Amongst others, thermalization in an inert buffer gas would be a suitable way to reduce the energy spread but requires a suitable arrangement for transferring these ions to high vacuum. The use of an Rf-only ring electrode assembly with decreasing inner diameter (aka ion funnel [3]), in combination with a convergent-divergent nozzle is currently studied as a method to thermalize laser-generated ions for mass spectrometric applications. This configuration provides a sufficient pressure drop between ion source and mass spectrometer, while allowing for multiple collisions and efficient ion cooling. At the same time, it significantly simplifies the configuration when compared with a conventional ion funnel with axial ion acceleration using a DC gradient [3,4]. Ion transfer through the funnel is determined by the supersonic expansion through the nozzle and the operating conditions of the ion funnel. Our first approach utilizes a 532-nm Nd:YAG nanosecond laser in order to characterize ion transmission as a function of ion funnel operating conditions during ablation of pure metal and alloy samples. The presence of the high pressure (mbar) buffer gas was found to not only reduce kinetic energy spread, but can also increase the overall peak duration of a single laser ablation event, which can mitigate space charge effects to some extent. Still, the ion transmission through the ion funnel showed a pronounced dependence on m/Q, as a result of the pseudostationary fields created near the ion funnel electrodes.

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LA-OL 2: LASER-ASSISTED ANALYSIS / GLOW DISCHARGE - GENERAL SESSION 2

Time: Thursday, 23/Feb/2017: 11:30am - 12:10pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Cornel Venzago

Session Chair: Lisa Fischer

11:30am - 11:40am

LA-OL 2: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Laser Ablation, Particle, Particle Size Distribution, ICP-MS

Formation of particles during laser ablation ICP-MS

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Laser ablation was performed by nanosecond laser ablation systems at the wavelength of 193 and 213 nm. Different materials and different ablation conditions were used for the study of the aerosol formed during laser beam-sample interaction and for the study of the ablation craters.

The particle size distribution (PSD) of dry aerosol was monitored simultaneously with LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) analysis using different aerosol spectrometers – Fast Mobility Particle Sizer (FMPS), Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS). The unique combination of LA-ICP-MS and FMPS offers the possibility of controlling the particle size distribution every 1 s of the ablation process in the size range of 5.6 – 560 nm.

Ablation craters were additionally studied using scanning electron microscope, digital microscope and energy dispersive X-ray analysis. The link between laser ablation conditions, particle formation and elemental fractionation was discussed.

Acknowledgements

The results of this research have been acquired within CEITEC 2020 (LQ1601) project with financial contribution made by the Ministry of Education, Youths and Sports of the Czech Republic within special support paid from the National Programme for Sustainability II funds.

11:40am - 11:50am

LA-OL 2: 2

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LIBS, LA-ICP-MS, polymer analysis, multivariate calibration

Analysis of minor and trace elements in polymers using Tandem LA/LIBS

Maximilian Bonta, Andreas Limbeck
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Nowadays, polymers are used in a wide range of scientific as well as industrial applications. Besides structural and molecular properties, also the concentrations of minor and trace metals in polymers are an important aspect. Increased metal concentrations can influence physical and chemical properties of the products, and especially heavy metals can pose problems for health and environment. Thus, accurate analysis of metals in polymer matrices is required.

Besides X-ray based techniques, where limits of detection are often insufficient, LA-ICP-MS is considered excellently suitable for high-sensitivity determination of a wide elemental range. However, matrix-matched standards are required to tackle the presence of matrix effects when analyzing different polymer types to achieve accurate quantification. Such matrix-matched standards are either commercially unavailable and need to be prepared in-house – which poses major workload –, or the analyzed polymer type is even unknown (*e.g.*, in recycling applications).

In this work, Tandem LA/LIBS instrumentation offering simultaneous sample analysis using LA-ICP-MS and LIBS was applied to tackle this problem. Minor and easily excitable elements (*e.g.*, Li, Na) were analyzed using LIBS, while trace elements could be monitored in the same run of analysis using LA-ICP-MS. Additionally, a wide-wavelength LIBS spectrum also provided information about the matrix composition of the sample by elemental and molecular emissions of the bulk components, further used for statistical data analysis to support multivariate calibration. Polymer layers with known element concentrations were prepared using spin coating, a technique which proved to be a fast and simple approach for the production of polymer standards. With thicknesses in the single digit µm-scale, the layers could even be used to quantify signal intensities obtained from bulk samples. Apart from successful element quantification, different polymers could be distinguished using their characteristic LIBS spectra, containing elemental, as well as molecular emission bands from the bulk polymer components. Trace metals in the polymers which were not accessible for stand-alone LIBS analysis were detected using ICP-MS. Using such combination of LIBS and LA-ICP-MS accurate quantification of trace elements in different bulk samples with known as well as unknown composition could be achieved.

11:50am - 12:00pm

LA-OL 2: 3

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Laser ablation, ICP-OES, polymers, optimization, calibration, crater, aerosol

QUANTITATIVE ELEMENTAL ANALYSIS OF POLYMERS BY LASER ABLATION-INDUCTIVELY COUPLED PLASMA

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Polymeric materials are increasingly being employed in different fields because they show important advantages such as their high adjustable properties or low production cost. Additives containing particular elements are usually incorporated to polymers in a wide range of concentrations. These additives are very important because their distribution influences the chemical and physical properties of the polymer.

Besides, it is worth mentioning that the polymers have to comply with a significant number of regulations to control the maximum amount of toxic heavy metals. Therefore, it is very important to develop analytical methods for carrying out elemental analysis of polymers. The most common techniques used for determination of metals in polymers are spectroscopic techniques such as ICP-OES or ICP-MS. However, these methods are time consuming and require the sample dissolution following complex procedures, which lead to the introduction of contaminants and loss of volatile components.

In order to minimize these problems, laser ablation-inductively coupled plasma-mass spectrometry can be used for the direct determination of additives in solid polymers. In fact, this technique allows analysis of all type of solid samples with minimal or no sample preparation. Besides, laser ablation is able to provide results on both bulk and localized analysis. However, one of the most important drawbacks of LA is related with the calibration. In this case, external calibration using matrix-matched solid standards is normally recommended. However, matrix-matched solid standards are often not available. Therefore, a new calibration method is necessary.

In the present work, several polymers were analyzed by LA-ICP-OES. The laser ablation system was a Q-switched Nd:YAG laser operated at 213 nm. The optimization of the laser operating parameters both in terms of sensitivity and elemental segregation was carried out for each matrix. In order to understand the ablation mechanism of polymers, results corresponding to crater and aerosol characterization by Secondary Electron Microscopy are also shown. A dried droplet calibration is suggested for carrying out quantitative analysis without using matrix-matched solid standards. This calibration is based on the deposition of several droplets, containing increasing elemental concentrations, on the polymer surface. Once the solvent of the droplets is evaporated, the dried solid deposits are ablated. The results show that this technique could be considered as a simple standard addition methodology for laser ablation.

12:00pm - 12:10pm

LA-OL 2: 4

Topics: Sample introduction and sample preparation, Elemental analysis

Keywords: Surface contamination, surface cleaning, Glow Discharge, Passivation layer

Investigation of the impact of surface cleaning procedures on near surface depth profiling using Glow Discharge Optical Emission Spectroscopy

Kjell Arne Bengtson, Mats Randelius

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Glow Discharge Optical Emission Spectroscopy (GD-OES) was applied for Compositional Depth Profiling (CDP) of passivation layers on stainless steels. The purpose of this work was to investigate the impact of surface cleaning procedures on the depth profiles of near surface layers in the few nm range.

Stainless steel samples were ground with dry Aluminium oxide paper to 220 Mesh, providing a reference assumed to have a minimum of surface contamination in the form of hydrocarbons and/or water. A few samples were intentionally contaminated with fingerprints. The contaminated samples were cleaned using different combinations of ethanol, aceton, isopropanol and blowing carbon dioxide gas onto the surface as the final step. The surface carbon was determined by GD-OES CDP on all samples quantified in units of mg/m^2. In order to minimise the impact of surface contamination on the CDP analysis of the oxide passivation layer, the depth profiles were also quantified excluding carbon. The elements included in the quantification were oxygen, iron, chromium, nickel, molybdenum, manganese and silicon. The shape of the quantified depth profiles were compared for the different states of surface cleanliness.

The results showed that the ground reference samples had 1 – 2 mgC/m^2; this could in fact be intrinsic contamination of the GDL but it is a very low value. The cleaned samples had greatly varying residual contamination in the range 5 – 50 mgC/m^2. The highest value was obtained with aceton rinsing followed by drying with hot air. The lowest value was obtained with isopropanol rinsing followed by drying with hot air and finally blowing the surface with carbon dioxide gas.

The near surface depth profiles of the passivation layers were significantly affected by contamination > 10 mgC/m^2, even when excluding carbon from the quantification. One reason is that any surface contaminant is likely to contain oxygen, and this content cannot be separated from the oxygen in the oxide. However, the presence of surface contamination is also detrimental to the near surface depth resolution. The obvious conclusion is that it is extremely important to device effective and reproducible surface cleaning procedures for near surface CDP analysis with GD-OES.

NANO-OL 2: NANOMATERIAL ANALYSIS - GENERAL SESSION 2

Time: Thursday, 23/Feb/2017: 11:30am - 12:10pm

Location: ARLBERG-well.com ARLBERGSAAL

Session Chair: Norbert Jakubowski

Session Chair: Andreas Zitek

11:30am - 11:40am

NANO-OL 2: 1

Topics: Elemental analysis, Nanomaterials, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Nanoparticles, Mass Cytometry, Single cell ICPMS

Quantification of AgNPs in single cells by Single Particle/Single cell inductively coupled plasma mass spectrometry and Mass Cytometry

Ana Lopez-Serrano Oliver[1], Sabine Baumgart[2], Andreas Gruetzkau[2], Norbert Jakubowski[1], Andrea Haase[3]

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According the recommended definition established by the European Commission, EC, (2011/696/EU) [1] nanoparticles (NPs) are natural, incidental or manufactured materials containing particles, in an unbound state or as an aggregate or as an agglomerate and where for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm. Among them, silver NPs (AgNPs) are being one of the most explored systems with various applications that include biomedical, pharmaceutic, catalytic, electronic, cosmetic applications [2]. However, little is known regarding their hazards for health and environment. Some studies have revealed that the same unique properties of metallic AgNPs could also be responsible for potential harmful effects on the environment and human health [3]. Currently, the assessment of their impact is hampered by limited analytical capabilities to detect them directly in complex biological matrix and new sensitive and selective analytical methods must be developed and validated in order to elucidate their toxicological effects prior to increase and promote the AgNPs production.

In this study, we tested two analytical methodologies based on inductively coupled plasma mass spectrometry (ICP-MS) for the first time to detect and quantify AgNPs at single cell level: Mass Cytometry (CyTOF) and Pneumatic nebulization coupled to ICP-MS working each in single cell/particle mode. The AgNPs uptake by individual cells such as THP-1 macrophages was monitored at two different AgNP concentrations, 0.1 and 1 mg L^{-1} after 4 and 24 h exposure. Silver signals measured by using both methodologies demonstrated that the uptake of AgNPs by THP-1 macrophages was dependent on exposure concentration and incubation time. The number of AgNPs per cell obtained by both approaches were in good agreement. Results were further validated by measuring the cell digest in liquid mode and subsequent calculation of the silver amount. .

Both analytical approaches enable the quantification of AgNP at single cell level while multi-parameter mass cytometry provides additional phenotypical information of the cells by using suitable metal labeled antibodies.

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11:40am - 11:50am

NANO-OL 2: 2

Topics: Nanomaterials, Environmental sciences

Keywords: Single-Cell-ICP-MS, nanoparticle, exposure, dose, response

Single Particle ICP-MS: quantifying exposure and dose of gold and silver NPs to freshwater alga

Ruth Corrin Merrifield[1], Chady Stephan[2], Jamie Lead[1]

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Exposure and dose of nanoparticles (NPs) to any single cell, has been a topic of discussion over many years. In the medical profession they want to know how much of a drug containing metals is actually entering the target cell and in the environment we want to know how much of a contaminant is entering single celled organisms, what effect they have and whether these are transported up the food chain. It is generally accepted that desirable metrics for measuring exposure and dose in this case would be particles per mL (part. / mL) and concentration per cell (conc. / cell) respectively. However because of instrument limitations these have both been measured using ionic mass concentration which means there is some vital missing information.

Here we exposed three strains of freshwater algae cell to Au NPs and Au ions. We show that single cell ICP-MS (SC-ICP-MS) was able to measure the number of NPs in the suspension media (exposure), the number of cells containing metal (% uptake) and finally the amount of metal within those cells (dose) in various different species of fresh water algae cell. We show that although the exposures are kept constant (ionic concentration of 1 ppb, equating to a NP concentration of around 500,000 part. / mL the dose and response is highly dependent on the algae strain.

11:50am - 12:00pm

NANO-OL 2: 3

Topics: Nanomaterials, Environmental sciences

Keywords: FFF, environmental matrices, sediment

Development and optimization of an extraction process for the semi quantitative determination of titanium dioxide nanoparticles in environmental samples using cFFF hyphenated to ICP-MS/MS

Florian Dutschke[1,2], Daniel Proefrock[1]

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Introduction

The continuously growing application of manufactured nanoparticles (NPs) in various sectors of human life raised growing concern about possible toxic and adverse effects in particularly for the environment due to interactions with such nanomaterials. Titanium dioxide (TiO_2) nanoparticles represent one of the most frequently applied nanomaterials with a production volume of at least 15 kt per year. Recent studies indicate that TiO_2 can lead to oxidative stress beside various adverse long term effects on different living organisms. Nevertheless to investigate the environmental impact of such particles, information about their concentration, size-distribution in different environmental compartments (e.g. water and sediment) is of great importance. Additionally, information about the elemental fingerprint of these particles is relevant to differentiate natural TiO_2 from manufactured nanoparticles.

Experimental

A centrifugal field flow fractionation (cFFF) system has been hyphenated to multi-angle-light-scattering (MALS) and inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) optimized for the separation and detection of TiO_2 NPs. Ti detection is strongly interfered by typical matrix elements, which are present in environmental samples. Therefore, an ICP-MS/MS method operated in the NH_3 mass shift mode has been developed to allow a sensitive and interference free detection of Ti in the investigated NPs. In addition, a process for the extraction of the nanoparticle fraction from sediment and water samples has been developed and optimized with respect to achieve a high recovery and good extraction reproducibility.

Results and discussion

The application of the NH_3 mass shift mode, allowed the detection of ^{48}Ti as $^{48}Ti(NH_3)_6$ at mass 150 at levels of about 7 µg L^{-1} even in the presence of several mg/L of Ca. To achieve good separation different parameters such as field strength, carrier solution composition, flow rate as well as the field strength program were optimized to provide well resolved fractograms for all kinds of TiO_2 NPs. The application of a rotation speed of 2500 rpm at 0.5 mL min^{-1} flow rate using water as carrier solution provides the best separation efficiencies for the different particles, allowing the accurate determination of their particle size distribution with a size detection limit of about 30 nm. To further characterize the different tested TiO_2 NPs their individual element fingerprint has been investigated after their total microwave assisted digestion. Beside Ti different other elements such as W, Pb, As or Al have been found in the different materials, which could be either impurities or parts of the coating causing their characteristic elemental fingerprint. Finally a new and optimized extraction process has been developed for the screening of nanoparticles in water and sediments with a very high spike recovery up to 95 % traceable to the TiO_2 NP reference material NIST SRM 1898.

12:00pm - 12:10pm

NANO-OL 2: 4

Topics: Elemental analysis, Nanomaterials

Keywords: Ti, TiO2, whole blood, nanoparticles, interference, clinical analysis, ICP-MS

The challenges of analysing Titanium and TiO2 nanoparticles in biological matrices

Dagmar Koller, Jonathan Powell

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The increased need to analyse titanium (Ti) in biological matrices at trace levels became prevalent for two main reasons. Firstly, the increased use of Ti-based prostheses came with the subsequent need to check for implant failure and release of Ti debris/ions into the blood stream. Secondly, there is considerable use of TiO_2 nanoparticles in a wide range of consumer products, including processed foods, nutraceuticals and pharmaceuticals. Understanding the absorption and bio-distribution of these particles is now of significant interest.

A wide range of analytical approaches have attempted to determine not just basal levels of Ti (and occasionally TiO_2) in biological fluids and tissues but, importantly, changes to the baseline. However, when comparing results from current literature it is apparent that there is a large variation of reported basal levels of Ti in biological matrices such as whole blood and serum, and that this in turn very likely effects the interpretation of changes to baseline. In other words, why some groups report no absorption of Ti following ingestion of TiO_2 particles, and others report significant absorption may be purely an analytical issue.

Here we carefully investigated the current publication landscape and, in collaboration with 6 specialist research laboratories in the field, conducted our own round robin studies to establish parameters which support unequivocal analysis of Ti in human whole blood.

We will present the findings of our collaboration in the context of the literature and provide some initial observations of the analysis of TiO_2 particles in whole blood by single particle ICP-MS/MS.

NANO-PL: NANOMATERIAL ANALYSIS - PLENARY LECTURE

Time: Thursday, 23/Feb/2017: 8:30am - 9:00am

Location: ARLBERG-well.com ARLBERGSAAL

Session Chair: Norbert Jakubowski

Session Chair: Andreas Zitek

8:30am - 9:00am

NANO-PL: 1

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials

Keywords: Nanoparticle analysis, AF4/ICP-SFMS, stable isotopes

ICP-MS - a powerful and versatile tool in “Nanolytics”

Björn Meermann[1], María Montes Bayón[2], Daniel Turiel Fernández[2], Thomas Ternes[1], Wolgang Tremel[3], Frank Vanhaecke[4], Kristina Wichmann[3]

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Downscaling materials to the size range of several nanometers can change their properties markedly and promising material characteristics opening new fields of application popped up during the last two decades - e.g. functionalized materials, medicine, food, cosmetics. Besides the beneficial properties of the new technology, questions regarding potential toxicological and environmental risks and behavior of nanomaterials (NMs)/nanoparticles (NPs) in complex matrices occurred. Thus, a clear definition was needed enabling obligation for indication of the presence of NMs/NPs especially in consumer goods. Hence, recently, the EC launched a definition on NMs/NPs [1]. However, categorizing NMs/NPs according to the EC definition as well as shed light on the behavior of NPs in complex matrices turned out to be a challenging task necessitating powerful and versatile analytical tools: (i) fractionation at the nanoscale, (ii) number-based quantification, (iii) tracing of NPs, and (iv) tackling complex matrices/sample preparation.

Following a brief introduction into the field of NPs, the first part of this plenary lecture focusses on state of the art analytical techniques for NP analysis linking current applications. After a general overview of different techniques, the broad applicability of techniques based on ICP-MS will be spotlighted. Focal points are placed on Field-Flow Fractionation (AF4, sdFFF) coupled on-line to ICP-MS [2], and the prospering technique of single particle ICP-MS [3, 4]. An emerging topic is the application of ICP-MS based techniques for bioimaging - thus, the use of LA-ICP-MS [5] as well as Mass Cytometry [6] in NP-cell studies will be highlighted. Besides this, a brief look will be taken on recent instrumental developments of ICP-MS, i.e. ICP-QQQ-MS and ICP-ToF-MS, and their relevance in NP analysis [7]. A further emerging field in NP analysis is isotopic analysis [8] - either for monitoring isotope fractionation effects during NP dissolution/formation [9], or for deploying isotopically enriched isotopes as tracers.

Within the second part the capabilities of stable isotopic tracers in NP analysis are presented - tracing stable isotope labelled NPs (^{57}Fe-labeled NPs) via AF4/ICP-SFMS spiked in a complex sediment slurry matrix filtrate [10].

References:

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NANO-IL 1: NANOMATERIAL ANALYSIS - INVITED LECTURE 1

Time: Thursday, 23/Feb/2017: 9:00am - 9:20am
Location: ARLBERG-well.com ARLBERGSAAL
Session Chair: Norbert Jakubowski
Session Chair: Andreas Zitek

9:00am - 9:20am

NANO-IL 1: 1

Topics: Nanomaterials, Plasma source fundamentals, instrumentation and mechanisms
Keywords: single nanoparticle analysis, inductively coupled plasma mass spectrometry, instrumentation

Nanoanalysis with Mass Spectrometry: On the Benefits of Microsecond Time Resolution in ICP-Q-MS

Carsten Engelhard, Ingo Strenge, Darya Mozhayeva
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In this presentation, recent developments in inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS) instrumentation for nanomaterials research will be reviewed and an approach for direct, fast, and high-throughput nanomaterial characterization on a single particle level will be presented.

In the first part of the presentation, the current state-of-the-art in single-particle (spICP-MS) for the detection and characterization of single nanoparticles (NP) will be reviewed. Also, a custom-built high-speed data acquisition (DAQ) unit specifically tailored to the needs of spICP-MS and CE-spICP-MS will be presented [1]. The DAQ was built in-house and enables continuous acquisition of signals from discrete ion clouds in the ICP with microsecond time resolution and 100% duty cycle. Fully time-resolved temporal profiles of individual single droplet or particle events can be recorded. The performance of this approach compared to conventional ICP-MS operation and selected applications will be discussed. Using a time resolution much higher than the typical duration of a particle-related ion cloud, the probability of measurement artifacts due to particle coincidence could be significantly reduced and the occurrence of split-particle events in fact was almost eliminated. Fully time-resolved temporal profiles of transient signals originating from single gold nanoparticles as small as 10 nm are presented. The advantages and disadvantages of millisecond *versus* microsecond dwell times are critically discussed including measurement artifacts due to particle coincidence, split-particle events, and particle number concentration.

Also, it will be discussed how separation methods coupled to ICP-Q-MS can aid the detection of NPs in complex mixtures. Specifically, a method that we developed for nanoparticle separation, size characterization, speciation, and quantification of gold and silver nanoparticles using capillary electrophoresis (CE) and ICP-MS [2] will be discussed and our recent efforts to expand this approach also to CE-spICP-MS will be presented.

References:

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NANO-OL 1: NANOMATERIAL ANALYSIS - GENERAL SESSION 1

Time: Thursday, 23/Feb/2017: 9:20am - 10:10am

Location: ARLBERG-well.com ARLBERGSAAL

Session Chair: Norbert Jakubowski

Session Chair: Andreas Zitek

9:20am - 9:30am

NANO-OL 1: 1

Topics: Nanomaterials, Environmental sciences

Keywords: single particle ICP-MS, engineered nanoparticles, enzymatic digestion

Single particle ICP-MS characterization of engineered nanoparticles uptake and bioaccumulation by edible plants

Justyna Wojcieszek[1], Javier Jiménez-Lamana[2], Lena Ruzik[1], Monika Asztemborska[3], Maciej Jarosz[1], Joanna Szpunar[2]

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Due to their unique physical and chemical properties, the use of engineered nanoparticles (ENPs) has exponentially increased in recent years causing their presence in the environment. As a consequence, ENPs can interact with plants and their impact on edible plants in the context of food safety needs to be investigated. Despite the rapid development of NPs applications, the mechanisms of plant penetration by ENPs are not well understood.

The main aim of the project was the development of analytical methodology for characterization of engineered nanoparticles in edible plants to get the knowledge about their uptake and bioaccumulation process. Enzymatic digestion method with Macerozyme R-10 was developed in order to release the largest amount of intact NPs from different parts (roots, stems and leaves) of studied plants. In the next step of the proposed project, SP-ICP-MS was used to determine the dissolved and nanoparticulated forms and define the differences in the uptake, distribution and degree of accumulation of NPs in edible plants. The influence of ICP MS acquisition parameters on the results obtained has been evaluated.

Obtained results show that depending on the chemical nature of NPs, they are distributed in various plant organs in different degrees as intact nanoparticles (as a result of metal NPs uptake and transport up to above ground organs) or can undergo transformation to dissolved forms of the metal. This information is essential from the point of view of food safety taking into account that different parts of the studied plants are edible. The developed methodology combining enzymatic sample digestion and SP-ICP-MS proved to be reliable and highly sensitive and can be used at an environmentally relevant trace concentration levels.

Acknowledgement: Project financially supported by the National Science Centre, Poland (grant no 2015/18/M/ST4/00257).

9:30am - 9:40am

NANO-OL 1: 2

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials

Keywords: Asymmetric flow field-flow fractionation, Quantum dots, Bioconjugates, Stoichiometry, Elemental mass spectrometry

Determination of the stoichiometry CdSe/ZnS quantum dot to antibody in bioconjugates by asymmetric flow field-flow fractionation coupled on-line to elemental mass spectrometry (ICP-QQQ)

Diego Bouzas-Ramos[1], Jorge Ruiz Encinar[1], José I. García Alonso[2], José M. Costa-Fernández[1], Alfredo Sanz-Medel[1]

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The development of sensitive bioanalytical applications of engineered metal nanoparticles demands for analytical tools able to guide the functionalization of their inorganic-core with biomolecule recognition units (such as antibodies, proteins and/or aptamers) as well as characterize and control this bioconjugation reaction of the nanoparticles to such recognition units, which are specific for the target biomolecules of interest.[1] Among the different metal nanoparticles popular today, photoluminescent quantum dots (QDs) stand out due to their exceptional and tunable fluorescent properties which enable their use as labels for biomedical applications, such as cell biology and immunoassay. However, such methods based on QDs are still not very reliable for quantitative measurements.

The analytical potential of QDs to be used as labels for the quantitative analysis of biomolecules will require for the control of the bioconjugation reaction and the determination of the number of antibodies or recognition units attached per nanoparticle.[2] In this context, the hybridation of the asymmetric flow field-flow fractionation (AF4), which is one of the most promising separation techniques able to achieve size-dependent separation of nanoparticles and biomolecules, with an inductively coupled plasma-mass spectrometry (ICP-MS) could provide invaluable capabilities and information to achieve the intended purpose.

In this work, the AF4 coupled on-line to ICP-MS is proposed as a powerful diagnostic tool for QDs bioconjugation studies. In particular, the determination of QDs stoichiometry in bioconjugates (between a monoclonal IgG antibody (Ab) and CdSe/ZnS core-shell QDs, which are surface-coated with an amphiphilic polymer) has been monitored by such hyphenated technique. Experimental conditions have been optimized searching for an appropriate separation between the sought bioconjugates from the eventual free QDs and antibodies excesses employed during the bioconjugation reaction. Moreover, an ICP-MS equipped with a Triple Quadrupole was selected as elemental detector to enable sensitive and reliable simultaneous quantification of the elemental constituents, including elements difficult to be quantified by ICP-MS such as sulfur, of the QD-Ab bioconjugates, and the free QDs and Ab.

The hybrid AF4-ICP-QQQ technique used provided nanoparticle size-based separation and elemental detection analysis that turned out not only to investigate in depth the bioconjugation process but also to determine and quantify the stoichiometry QD:Ab in different bioconjugates assessed (including a commercially available sample of QD conjugates). That is a key challenge in future development of bionanoanalytical applications of such fluorescent QDs.

References

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9:40am - 9:50am

NANO-OL 1: 3

Topics: Nanomaterials

Keywords: SP-ICP MS, nanoparticles, substrate-assisted laser desorption, SALD, laser desorption

Laser-Assisted Introduction of Nanoparticles to ICP MS

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Introduction

Because of their rapid uptake, unknown distribution pathways and potential interactions in biological systems, nanoparticles (NPs) present a growing concern of environmental scientific community. Single particle inductively coupled plasma mass spectrometry (SP-ICP MS) has become and established tool for NP detection and characterization. In this contribution, we report a new sample introduction technique of NPs to SP-ICP MS.

Methods

Suspension of hundreds gold or silver NPs in 200 nL droplets is deposited and dried on a strongly absorbing plastic plate (polyethylene terephthalate glycol), which is ablated with 213 nm laser (UP 213, New Wave Research) at a relatively low fluence (~0.2 $J \cdot cm^{-2}$). The generated aerosol is delivered to an ICP quadrupole mass spectrometer (7500 CE, Agilent Technologies).

Results and conclusions

The technique substrate-assisted laser desorption (SALD) was originally developed for analysis of sub-microliter volumes of dissolved inorganic species. We demonstrate that individual intact NPs can be efficiently desorbed from the plastic surface with the UV laser. SALD ICP MS was validated using well characterized, reference gold NPs. Experimental conditions, such as the laser fluence, sample scan rate, carrier gas type and flow rate were carefully optimized to maximize transport efficiency and NP signal. The transport efficiency exceeded 60 % under optimal conditions. A portion of NPs is shown to disintegrate at higher laser fluence (~6 $J \cdot cm^{-2}$). Quantification of NP number concentration and determination of NP size in other samples was performed. The results were compared with those obtained using the conventional nebulizer SP-ICP MS.

Acknowledgement

We gratefully acknowledge the financial support of the Czech Science Foundation (GA15-05387S) and the project CEITEC 2020 (LQ1601) of the Ministry of Education, Youth and Sports of the Czech Republic.

9:50am - 10:00am

NANO-OL 1: 4

Topics: Nanomaterials, Environmental sciences

Keywords: Lactuca Sativa, Silver Nanoparticles, SP-ICP-MS, Enzimatic digestion.

Exposure of Lactuca sativa to silver nanoparticles: Characterization of their uptake and translocation by Single Particle Inductively Coupled Plasma Mass Spectrometry.

Laura Torrent, Eva Marguí, Manuela Hidalgo, Mònica Iglesias

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In recent years, the use of manufactured nanoparticles has increased considerably in different types of commercial products. This increase has raised concerns about effects of these materials on the environment and health. Silver nanoparticles (AgNPs) are one of the most used nanomaterials due to its antibacterial activity and have been incorporated in various areas like food technology, medicine or textiles. The growth in applications of AgNPs increases inevitably their release to the environment. One of the main routes of entry of these nanomaterials into the environment is through the use of sewage sludge as fertilizer in agricultural lands. From soils, AgNPs can interact with plants which could gain access to the trophic chain.

In order to assess the transference of AgNPs to plants, *Lactuca Sativa* was cultivated in hydroponic medium containing either ionic silver or AgNPs. In this study AgNPs with different sizes and coatings (citrate, polyethylene glycol or polyvinylpyrrolidone) were compared. *Lactuca Sativa* plants were grown during nine days in lab-controlled conditions. Afterwards, two digestion methods were applied to vegetal samples (roots and leaves): microwave acid digestion, which allows the total silver determination, and enzymatic digestion, which allows maintaining the silver nanoform. The resulting digests were analysed with inductively coupled plasma optic emission spectrometry (ICP-OES) for total silver determination. The enzymatic digests were also analysed with single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) to ascertain their form.

Exposure experiments of *Lactuca Sativa* to AgNPs indicated that there were no significant differences of silver content in the plant when using different coated particles. Experiments carried out with ionic silver showed higher accumulation in the roots but less translocation to the aerial part than those with AgNPs. Experiments performed varying the AgNPs concentration indicated that an increase of the silver concentration rises the accumulation of silver in the plant until a certain value. The evaluation of the influence of particle size in absorption of AgNPs to plants showed that small particles were more accumulated in the roots but less transported to the leaves than large particles.

SP-ICP-MS analysis of enzymatic digests revealed that AgNPs maintain partially their nanoform in roots for all experiments carried out using nanoparticles of different coatings, sizes or concentrations. However, their presence in leaves could not be confirmed in the majority of the experiments.

In summary, AgNPs are assimilated by roots and transported to the leaves of *Lactuca Sativa* regardless of particle size, coating and concentration. Nanoparticles are less assimilated but more translocated to the aerial part of the vegetal than ionic silver. SP-ICP-MS confirmed that AgNPs maintain their form in the roots.

10:00am - 10:10am

NANO-OL 1: 5

Topics: Nanomaterials

Keywords: nanoparticles, single particle ICP-MS, sample preparation, food, biological samples

Single particle ICP-MS for the detection of inorganic nanoparticles in food and biological samples

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Inductively coupled plasma-mass spectrometry in single particle mode (single particle ICP-MS) has become a frequently used method for the detection and characterization of inorganic nanoparticles. The technique has been applied in our laboratory for studying inorganic nanoparticles in a variety of biological samples, including rat lung and liver tissue (gold and cerium oxide NPs), whale brain and liver tissue (mercury selenide NPs), human synovial fluid (cobalt and chromium-containing NPs) and human placenta tissue (silver NPs). Furthermore, food-related samples were investigated including lean chicken meat (silver NPs), game meet (lead NPs), food simulants (silver NPs), and noodles (aluminum-containing NPs).

We identified sample preparation as the most crucial step, especially in the case of solid / semi-solid matrices where simple dilution is not sufficient. As single particle ICP-MS analysis is not as sensitive as other analytical techniques, like field flow fractionation, to eventually remaining matrix residues, complete digestion of the matrix is usually not required. The main challenge is to minimize changes of the NPs during sample preparation mainly due to dissolution. For the majority of examples, we identified enzymatic digestion as the most suitable sample preparation method.

Our experiences show that single particle ICP-MS is a powerful screen method for the presence of NPs, but that care has to be taken with regards to false-positive-results and the obtained quantitative information in terms of particle size distribution and number / mass concentration. False positive results were obtained for two reasons: 1) Induced particle formation during sample preparation, e.g. from ionic species and 2) carry-over. For the latter case, we observed that analysis of ultrapure water between samples was not sufficient for evaluating carry-over, but that a realistic reagent or blank sample needs to be analyzed. Matrix-matching of calibration solutions was not possible in every case due to instability of the ionic species. In these cases, ionic standards had to be analyzed in ultrapure water or diluted acidic acid.

Based on our experiences, the talk will highlight the challenges and the “lessons learned” in relation to sample preparation for single particle ICP-MS, determination of transport efficiency, calibration, and data interpretation, and the next steps in the current and future work described.

NANO-IL 2: NANOMATERIAL ANALYSIS - INVITED LECTURE 2

Time: Thursday, 23/Feb/2017: 10:50am - 11:30am

Location: ARLBERG-well.com ARLBERGSAAL

Session Chair: Norbert Jakubowski

Session Chair: Andreas Zitek

10:50am - 11:10am

NANO-IL 2: 1

Topics: Nanomaterials, Environmental sciences

Keywords: multi-element single particle ICP-MS, engineered nanoparticles, environment, consumer products

Quantification and Identification of Nanoparticles in Consumer Products and the Environment

Frank von der Kammer[1], Antonia Praetorius[1], Milica Velimirovic[1], Andreas Gondikas[2], Jana Navratilova[3], Alexander Gundlach-Graham[4], Eli Goldberg[4], Detlef Guenther[4], Thilo Hofmann[1]

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The analysis of ENPs in consumer products and environmental compartments requires different approaches and has to answer fundamentally different questions. While in products it might be required to produce a quantitative particle size distribution of a known ingredient which is present in comparable high concentrations, analysis in the environment requires the identification of an ENP to be of industrial, manufactured origin often at very low concentrations. In products the analysis has to provide data compatible with existing or future definitions or regulations (e.g. number or mass-based particle size distributions) while in the natural environment it is of more interest which types of NPs are present and which of those are manufactured even though the exact type or composition of the ENPs are unknown. Depending on the type of ENPs and the chemistry of the matrix methods could be extremely simple (Au-NPs in drinking water) or relatively complex (TiO_2 and Fe_3O_2 in sunscreen). We have developed methods for cosmentics, food and soils/waters using specifically adapted sample preparation techniques and quantification with classical Field Flow Fractionation-ICPMS, single particle techniques (EM and ICPMS) and for the first time multi-element single particle fingerprinting with ICP-TOFMS. Methods have been optimized for maximum recoveries in all steps of the analysis and qualified against original ENP samples before addition to the marketed products. This presentation will summarize the results from method development and is aiming to critically assess the different advantages and drawbacks of the methodologies for the different tasks in cosmetics, food and environmental sectors. Emphasis is on the new concepts and analytical requirements for fully simultaneous multi-element single particle TOF-ICPMS and the application of this technique to identify ENPs on the background of similar non-manufactured particles. Pitfalls emerging from truly simultaneous aquisition of short-lived transient signals will be discussed.

11:10am - 11:30am

NANO-IL 2: 2

Topics: Sample introduction and sample preparation, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Imaging mass cytometry

Highly multiplexed imaging of tissues with subcellular resolution by imaging mass cytometry

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Cancer is a tissue disease. Heterogeneous cancer cells and normal stromal and immune cells form a dynamic ecosystem that evolves to support tumor expansion and ultimately tumor spread. The complexity of this dynamic system is the main obstacle in our attempts to treat and heal the disease. The study of the tumor ecosystem and its cell-to-cell communications is thus essential to enable an understanding of tumor biology, to define new biomarkers to improve patient care, and ultimately to identify new therapeutic routs and targets.

To study and understand the workings of the tumor ecosystem, highly multiplexed image information of tumor tissues is essential. Such multiplexed images will reveal which cell types are present in a tumor, their functional state, and which cell-cell interactions are present. To enable multiplexed tissue imaging, we developed imaging mass cytometry (IMC). IMC is a novel imaging modality that uses metal isotopes of defined mass as reporters and currently allows to visualize over 50 antibodies simultaneously on tissues with subcellular resolution. In the near future we expect that over 100 markers can be visualized.

We applied IMC for the analysis of breast cancer samples in a quantitative manner. To extract biological meaningful data and potential biomarkers from this dataset, we developed a novel computational pipeline geared for the interactive and automated analysis of large scale, highly multiplexed tissues image datasets. Our analysis reveals a surprising level of inter and intra-tumor heterogeneity and identify new diversity within known human breast cancer subtypes as well as a variety of stromal cell types that interact with them.

In summary, our results show that IMC provides targeted, high-dimensional analysis of cell type, cell state and cell-to-cell interactions within the TME at subcellular resolution. Spatial relationships of complex cell states of cellular assemblies can be inferred and potentially used as biomarkers. We envision that IMC will enable a systems biology approach to understand and diagnose disease and to guide treatment.

NANO-OL 3: NANOMATERIAL ANALYSIS - GENERAL SESSION 3

Time: Thursday, 23/Feb/2017: 1:50pm - 3:40pm

Location: ARLBERG-well.com ARLBERGSAAL

Session Chair: Norbert Jakubowski

Session Chair: Andreas Zitek

1:50pm - 2:00pm

NANO-OL 3: 1

Topics: Nanomaterials

Keywords: Single particle, nanomaterials, nanoparticles, complex samples

Single Particle ICP-MS: Keeping the feet on the ground

Francisco Laborda[1], Isabel Abad-Alvaro[1], Eduardo Bolea[1], Juan R. Castillo[1], Miguel A. Gomez-Gonzalez[2], Javier Jimenez-Lamana[3], Joanna Szpunar[3]

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Six years ago, single particle ICP-MS (SP-ICP-MS) was all but unknown by the ICP-MS community. In 2003, Degueldre and Favarger published their seminal paper establishing the basics of SP-ICP-MS, although it took several years to rediscover the technique. The trigger for this relaunching has been the emergence of engineered nanomaterials and the need for analytical methods in this field.

The development of SP-ICP-MS can be considered similar to that undergone by the ICP-MS technique itself. After the conception of the idea and the publication of the first papers, manufacturers launched commercial instruments rapidly. In this case, within a time span of three years all the ICP-MS manufacturers have got on board of SP-ICP-MS, launching instruments with improved specific performance for single particle detection and/or implementing new software for data processing. At present, SP-ICP-MS can be considered technically well supported by the available instrumentation, although more work would still be required on methodology and validation.

When looking at the scientific publications and manufacturer's reports, the perception is that SP-ICP-MS is out to solve almost any problem related to inorganic nanomaterials. Its capability to provide information about size (in fact, mass per particle), number concentration and elemental composition seems to justify that. However, almost 50% of the publications in the last five years covers fundamental aspects of the technique and about 85% involves the use of tailored synthetic nanoparticles, both as spikes or in different types of *in vitro* or *in vivo* experiments. On the other hand, real-world applications with unknown particles are still scarce. The reason does not lie in the attainable number concentration detection limits (down to 1000 particles mL^{-1}), but in its particle size detection limits (around 10 nm for a solid, pure, spherical and metallic particle). The key point is that detection of a particle depends on its composition, the element monitored, the presence of dissolved species of this element, the background level of the isotope measured and the detection efficiency of the instrument used. The practical consequences of this weakness are that, in real-world applications, SP-ICP-MS is mostly used as a screening tool, just capable of detecting the presence of particulate as well as dissolved species of an element, and providing size information when other ancillary techniques are used.

Different examples of real-world analytical problems faced by the authors, including testing of nanomaterials, mobilization of toxic elements in environmental conditions and the detection of biogenic particles, will be presented. The aim of the lecture is to reflect on the direction SP-ICP-MS is taking, the way ahead to become a mature technique and the reliable information that it can provide on a rational basis.

This work was supported by the MNECO/FEDER project CTQ2015-68094-C2-1-R.

2:00pm - 2:10pm

NANO-OL 3: 2

Topics: Nanomaterials

Keywords: Nanoparticles, flow injection, single particle inductively coupled plasma mass spectrometry

Characterization of 3-nm (and smaller?) metal nanoparticles by inductively coupled plasma mass spectrometry with and without flow injection

Ram P. Lamsal[1], Gregory Jerkiewicz[1], Steve Baranton[2], Christophe Coutanceau[2], Diane Beauchemin[1]

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In recent years, single particle inductively coupled plasma mass spectrometry (spICPMS) has emerged as a reliable tool for measuring the mass of nanoparticles (NPs) suspended in aqueous medium. Furthermore, if the shape, density and composition of NPs are known, their mass can be converted into sizes, and a size distribution can then be obtained. For the approach to provide accurate results, the suspension should be diluted enough that there is at the most one NP per droplet formed during nebulization, and the dwell time should be selected so as to measure only one NP at a time. Under these conditions, most ICPMS instruments operated in time-resolved mode can detect individual NPs as spikes in the steady-state signal. In this presentation, we will compare the performance of spICPMS to that of a simpler method involving flow injection (FI) of a discrete volume of sample or standard, i.e. FI-spICPMS.

FI-spICPMS is advantageous over spICPMS as it does not require measurement of the transport efficiency and of the sample uptake rate in order to measure the mass of NPs. It also only requires measurement of the transport efficiency for the conversion of mass into size. Moreover, the FI way of measuring the transport efficiency is not subject to variations in sample uptake rate as long as the whole injected volume is measured. These important advantages are in addition to other features of FI: high sample throughput, reduced matrix effects from the dispersion that is inherent to the FI process, reduced memory effect from the continuous washing afforded by the carrier, etc.

Both methods were applied to the measurement of pure platinum NPs having nominal diameters of 3 and 10 nm respectively, as measured by transmission electron microscopy (TEM). The mean of the corresponding NP size distributions obtained by spICPMS were calculated to be 3.5 ± 0.6 nm and 14 ± 3 nm respectively (n=3), in good agreement with TEM measurements. Furthermore, the corresponding size detection limits were 2 and 8 nm respectively. With FI-spICPMS, the mean NP sizes were calculated to be 3.0 ± 0.4 nm and 11 ± 2 nm respectively (n=3), in excellent agreement with the TEM measurements. The size detection limits obtained were 2 and 7 nm respectively. Hence, there is no degradation of performance when using FI-spICPMS instead of spICPMS.

To the best knowledge of the authors, no one has ever measured NPs so small by spICPMS. Such low detection limits are possible because of the high sensitivity afforded by the Varian 820MS quadrupole-based ICPMS instrument used for the above measurements, which features an ion mirror to reflect and focus the ion beam away from the plasma into a quadrupole located at a 90° angle. In theory, the measurement of even smaller NPs should be possible with a more sensitive instrument. This hypothesis will be tested with a PlasmaQuant Elite ICPMS instrument (from Analytik Jena). Very recent results obtained on such an instrument will thus also be presented.

2:10pm - 2:20pm

NANO-OL 3: 3

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Nanomaterials
Keywords: LA-ICP-MS, elemental bioimaging, nanomaterials in biological tissue

Imaging of Cerium Oxide Nanoparticles in Rat Lung Tissue by Means of LA-ICP-MS

Dörthe Dietrich[1], Antje Vennemann[2], Martin Wiemann[2], Michael Sperling[1,3]

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Cerium oxide nanoparticles are used in a wide range of applications, for example in catalysis or solar cells. They are also used as automotive fuel additives in order to increase the combustion efficiency. Therefore, a possible way of exposure to humans is the uptake by inhalation via ambient air. Knowledge about the distribution of the nanoparticles in the relevant organs can help to understand potential toxicity. To reveal the distribution of the particles in the lung of laboratory rats after application, the imaging technique laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is applied.

Different doses of cerium oxide nanoparticles were intratracheally instilled into rat lungs. The lung was removed after 3, 21 and 90 days and cryo-sections with 7 µm thickness were prepared. Formalin fixed tissue was investigated in parallel. Ablation was performed line-by-line with a 213 nm Nd:YAG laser using a spot diameter of 50 µm and subsequent merging reveals the distribution of cerium in the tissue. For quantification, standards based on gelatin were prepared containing different concentrations of cerium. The external calibration shows a good linear correlation between intensity and deployed concentration in the range from 1 to 5000 µg/g cerium.

Cerium was detected throughout the lung parenchyma and the overall concentrations depended on exposure concentration of nanoparticles. Cerium distribution patterns changed over time and indicated progressive compartmentalization. Alveolar macrophages were labelled immunohistochemically with FITC- and colloidal gold-coupled antibodies and, by this, identified via LA-ICP-MS at high spatial resolution of 5 µm spot size. This allowed to quantify the amount of cerium nanoparticles inside alveolar macrophages under in vivo conditions.

The study shows that LA-ICP-MS is well suited to quantify cerium in tissue sections and to correlate the cerium concentration to biological structures.

2:20pm - 2:30pm

NANO-OL 3: 4

Topics: Nanomaterials

Keywords: aflatoxin M1, milk, immunoassay, nanoparticles, inductively coupled plasma mass spectrometry

EVALUATION OF DIFFERENT INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY-BASED IMMUNOASSAYS FOR THE DETERMINATION OF AFLATOXIN M1 IN MILK

Emma Pérez Hernández, Guillermo Grindlay Lledó, Francisco Marco de la Calle, Pascual Martínez Peinado, Juan Mora Pastor

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Aflatoxins are secondary metabolites produced by different filamentous fungi known to represent a high risk for human health due to their mutagenic and teratogenic effects. These substances can be found in different kinds of food and animal feeds that have been in contact with fungi through the food chain under high temperature and humidity conditions. Different worldwide regulatory authorities have established very strict policies to limit the maximum aflatoxin levels in foods (50-500 ng/Kg) and highlight the need to develop new and more sensitive methodologies to quantify these toxins. The analysis of these substances is usually carried out by means of immunoassays due to their high sample throughput, specificity and simplicity.

Over the years, the use of inductively coupled plasma mass spectrometry (ICP-MS) as a detector in immunoassays for proteins and biomolecules has raised up significantly since it is quite straightforward to functionalized antibodies with elements detectable by this technique. The main advantages of ICP-MS in this type of application are: (i) specificity; (ii) compound-independent detection sensitivity; (iii) high elemental sensitivity; (iv) robustness; and (v) multiplexing capabilities. In a previous work we developed a new procedure to quantify aflatoxin M1 (AFM1) in milk samples by ICP-MS. The proposed methodology is based on a competitive immunoassay using secondary biotinylated antibodies and streptavidin-Au nanoparticles followed by Au detection by ICP-MS. Although the methodology was able to determine AFM1 at the security levels required by the current international policies with accuracy and precision, more sensitive methodologies are needed in order to be able to decrease the low maximum levels required.

The goal of the present work is to develop new analytical methodologies for the analysis of AFM1 using ICP-MS-based immunoassays. To this end, different competitive immunoassay strategies (namely, (i) Antibody Binding Inhibition Assay; (ii) Capture Bridge Inhibition Assay and (iii) Capture Inhibition Assay) and heteroatom-functionalized antibodies with gold and silver nanoparticles of different size have been developed. Experimental results show that, by the appropriate selection of the immunoassay procedure, the heteroatom tracer and the ICP-MS experimental conditions, the limit of detection of AFM1 can be reduced down to 0.1 ng/Kg. This value is one order of magnitude lower than the most sensitive immunoassay procedures described in the literature. Method accuracy and precision was successfully validated by analyzing an AFM1 certified reference material and spiked milk samples. AFM1 recovery values ranged from 80% to 102% whereas precision was lower than 10-15%.

Acknowledgements.

The authors would like to thank the Generalitat Valenciana (Project GV/2014/138) and the Vice-Presidency for Research of the University of Alicante (Project GRE12-19) for financial support of this work.

2:30pm - 2:40pm

NANO-OL 3: 5

Topics: Nanomaterials

Keywords: Single particle ICP-MS, Nanoparticle, Microalgal cell, Uptake, Adsorption

Characterization of nanoparticles uptake and adsorption by red microalgal cells using single particle ICP-MS

Shin-ichi Miyashita[1], Hiroaki Mitsuhashi[2], Shin-ichiro Fujii[1], Mitsuru Abo[2], Akiko Takatsu[1], Kazumi Inagaki[1]

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While nanoparticles (NPs) have been extensively used in various industrial and consumer products due to their unique physical and chemical properties, the inevitable release of the NPs to the environment through various waste streams has caused ecological concerns. Some previous model studies using microalgae, which are the dominant primary producer in most aquatic environments, have shown that some NPs have cytotoxic activity. However, details on mechanisms of their toxicity expression are poorly understood, although possible mechanisms have been proposed, such as cellular uptake and adsorption of NPs themselves or ions dissolved from NPs, cellular association of NPs, and effect of NP aggregates on the cells.

The objective of this study was to investigate possible interaction of NPs with microalgae, which might trigger their cytotoxic activity, through characterization of NPs uptake and adsorption by the thermo-acidophilic unicellular red alga *Galdieria sulphuraria* using single particle ICP-MS (spICP-MS). Different types of NPs (i.e., ZrO_2-NPs, Ag-NPs, Pt-NPs and Au-NPs with nominal diameters of <100 nm, 60 nm, 70 nm and 60 nm, respectively) and their respective salts were used in short-term (2 h) exposure experiments for the microalgal cells sterilely cultured in a medium under acidic (pH 2.5) or neutral (pH 7.0) condition. The spICP-MS was applied to obtain time-resolved spectra of NP- or salt-exposed cells after appropriate separation, and the resultant spectra were transformed into peak area-based frequency histograms to understand the differences in the uptake and adsorption of the NPs or salts by the cells.

As a result of analyzing the NP-exposed cells by spICP-MS, short transient signals derived from individual NP events in the plasma were detected only for Zr and Ag under either acidic or neutral exposure condition, indicating that both NP types can be taken up by the cells or adsorbed onto the cell surface. In addition, based on the comparison with the analytical results for the salt-exposed cells, the ZrO_2-NPs were mainly present in the form of particles, while the Ag-NPs were mostly present in the form of partially dissolved particles or dissolved ions. These results indicate that in contrast to Pt-NPs and Au-NPs, ZrO_2-NPs and Ag-NPs have high potential to interact with microbial cells. This information is important for understanding the early stage of the toxicity expression mechanisms of the NPs. In this presentation, analytical results of the dissolution and aggregation behavior of the NPs themselves in the presence or absence of the microbial cells will be additionally presented in connection with the above results.

2:40pm - 2:50pm

NANO-OL 3: 6

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials

Keywords: Nanoparticles, Asymmetric flow field-flow fractionation, Chemical oxidation, Toothpaste, Metal oxide particles.

Simultaneous on-line detection of SiO2, TiO2 and Al2O3 particles in toothpaste by asymmetric flow field-flow fractionation hyphenated to inductively coupled plasma mass spectrometry

Manuel Correia, Katrin Loeschner

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Toothpaste is a complex mixture of chemicals including e.g. emulsifiers, surfactants, and particles such as SiO_2, Al_2O_3 (abrasives) and TiO_2 (pigment), which can be nano or micrometer sized. During its normal use, a fraction of toothpaste may be swallowed and thus the individuals may be exposed to these metal oxides. The size of the particles is a determining factor for their biological fate and possible intestinal uptake. Therefore, in order to characterize these nano or microparticles, a method of analysis was developed aiming at simultaneous size separation of all three types of particles by asymmetric flow field-flow fractionation (AF^4).

Two sample preparation strategies were tested for analysis by AF^4: a simpler approach involving dilution of the toothpaste in aqueous solution and a more complex procedure consisting of microwave-assisted oxidation of the toothpaste matrix with hydrogen peroxide. Multi angle light scattering (MALS) was used for on-line size determination of the eluting particles and inductively coupled plasma mass spectrometry (ICPMS) was exploited for selective detection of SiO2, TiO_2 and Al_2O_3 particles.

The simpler sample preparation approach, matrix dilution, was found to be unsuitable for analysis of the toothpaste particles by AF^4 resulting in unusual elution profiles and low recoveries. The more complex procedure involving chemical oxidation of the matrix was found to be crucial for separation and detection of the toothpaste particles. The obtained channel recovery based on the MALS detector was satisfactory (>80%), and this procedure was selected for further AF^4 method development. The AF^4 method was optimized for optimal recovery and particle separation in terms of carrier liquid composition, cross-flow regime and focus conditions. The mass-based particle size distributions of Al_2O_3 and TiO_2 particles were obtained based on the ICPMS signal and after calibration of the AF^4 channel with polystyrene particle size standards. Triple-quadrupole ICPMS was used for detection of SiO_2 particles and was invaluable for obtaining additional information on this particle type. The Al_2O_3 and TiO_2 particle mass concentration was determined based on the AF^4-ICPMS fractograms using post-channel calibration with elemental standards and internal standardization. The obtained values were compared with the mass concentrations determined by ICPMS following microwave-assisted digestion of the toothpaste with hydrofluoric and nitric acid.

AF^4-MALS-ICPMS was found to be a powerful method for separating and estimating the size of the particles present in the toothpaste. This talk will describe the methodological steps required for analyzing the three distinct constituent particles and highlight the challenges related to sample preparation, AF^4 separation and ICPMS detection.

Acknowledgment: The work leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement n° 604347.

2:50pm - 3:00pm

NANO-OL 3: 7

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials, Metrology in chemistry
Keywords: ICP-MS, field flow fractionation, tattoo, health, metals

Characterization of metallic nanoparticles in tattoo ink using Asymmetrical Flow Field-Flow Fractionation coupled with ICP-MS

Robert Reed[1], Soheyl Tadjiki[1], Tony Pfaffe[2], Evelin Moldenhauer[2], Thorsten Klein[2]

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Field-Flow Fractionation-ICP-MS is a powerful analytical technique that can be used for characterization of nanomaterials. As a hyphenated system, FFF-ICP-MS generates elemental-based size distribution over a broad size range. It can also provide elemental molar ratio distribution which helps to study particles chemical composition as a function of particle size.

TiO2 nanoparticles are added to tattoo inks to enhance color strength. Commercial ink products containing non-metal colorants can be contaminated by traces of toxic metals. For example, cutaneous allergies may occur due to the presence of Ni in inks.

This presentation demonstrates the use of Asymmetrical Flow FFF coupled with ICP-MS to study various kinds of tattoo ink. Particle size and elemental distributions of various metals are measured to study the composition of ink ingredients as a function of particle size.

NANO-OL 3: 8

Topics: Nanomaterials

Keywords: Field Flow Fractionation, Inductively Coupled Plasma Mass Spectrometry, particulate Carbon, Latex particles

Extension and validation of FFF online with ICP-MS for the quantification of carbon in natural and engineered (nano)particles

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The online hyphenation of field flow fractionation (FFF) with inductively coupled plasma mass spectrometry (ICP-MS) is a flexible approach for quantitative size resolved determination of the elemental composition of (nano)particles. Multi-element capability enabled a broad range of applications for metallic nanoparticles and metal containing natural particles. However, in many cases both natural nanoparticles (e.g. humic acids) and engineered nanoparticles (e.g. polymer coated particles) contain also carbon as an element of major interest. Therefore, our work is focusing on particulate carbon determination using FFF-ICP-MS, which is a new application, to address this need without requirement of additional detectors.

Our recent work demonstrated the feasibility of carbon determination in natural water samples using FFF-ICP-MS and in parallel FFF online with an organic carbon detector (OCD) for method validation [1]. In this case the nanoparticles were mainly humic acids, i.e. organic macromolecules in the low nanometer range, which are likely to decompose in the plasma.

However, engineered particles, e.g. polymer particles, typically range from nanometer size up to low micrometer size and form more stable structures. Our current research investigates the performance of particulate carbon determination using FFF-ICP-MS for such polymeric engineered particles. As a model we selected commercial latex particle standards of different sizes ranging from approximately 20 to 750 nm. Carbon quantification is performed by ICP-MS in flow injection and FFF separation mode to study recoveries and potential particle size dependent effects. Initial quantitative results obtained in flow injection mode indicate adequate precision of replicate measurements and similar recoveries for all particle sizes in the range of 70 to 85% based on the polymer concentration given by the manufacturer. Further optimization and validation will be performed and presented as well as the application to further engineered carbon containing particles. Current results indicate that FFF-ICP-MS has the potential for quantitative multi-element determination of particles including also carbon which opens up a broad range of new applications.

[1] V. Nischwitz, N. Gottselig, A. Missong, T. Meyn, E. Klumpp, *J. Anal. At. Spectrom.*, 31 (2016) 1858-1868

BI-PL: BIOIMAGING - PLENARY LECTURE
(sponsored by ThermoFisher Scientific)

Time: Thursday, 23/Feb/2017: 1:50pm - 2:20pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Andreas Limbeck

Session Chair: Luca Bamonti

1:50pm - 2:20pm

BI-PL: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: bioimaging, single cell analysis, single particle analysis, immunoassays, medical diagnosis

THE QUANTITATIVE ELEMENTAL MICROSCOPE: FOR WHAT IS IT GOOD FOR?

Norbert Jakubowski[1], Heike Traub[1], Diego Estéban-Fernández[1], Simone Hösl[1], Ulrich Panne[1], Daniela Drescher[2], Tina Büchner[2], Janina Kneipp[2], Irene Moraleja[3], Guido Sauter[4], Hartmut Schlüter[4], Ronald Simon[4], Boris Neumann[5]

[1]Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany; [2]Humboldt-University of Berlin, Department of Chemistry, Berlin, Germany; [3]Universidad Complutense de Madrid, Madrid, Spain; [4]University Medical Center Hamburg-Eppendorf, Hamburg, Germany; [5]Proteome Factory AG, Berlin, Germany; norbert.jakubowski@bam.de

Elemental imaging of biological samples (bio-imaging) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) provides spatially resolved information on element distribution in thin sections of -tissues or cells. By rastering with a laser across the sample, a two-dimensional image of the elemental distribution can be achieved for all elements of interest. Using overlapping laser shots the area ablated from single cells or thin sections (5 to 10 µm) can be reduced significantly so that the pixel size of the intensity measurement is significantly reduced. Having in mind that a laser shot ablates a thin biological samples completely, we can make use of a new concept for calibration in the laser ablation method: the concept of total consumption. This new calibration strategy allows production of simple matrix matched standards and provides an internal standard by the ink jet technology, where a metal containing inks is used to print the calibration standard and the internal standard in a thin layer on top of the biological sample.

Different applications will be presented in this lecture where our calibration and internal standardization concepts have been applied. In the first example we used nanoparticle suspension of given particle numbers to quantify the up-take of metallic nanoparticles by biological cells. In the second example biomarkers (antibodies) have been tagged by metals to measure protein expression in prostata cancer. In this approach application of house keeping proteins are investigated additionally to compensate variations in thickness and density of the biopsy samples. In the third application different nephrotoxic behaviour of cisplatin, carboplatin, and oxaliplatin has been investigated in a mice model to study the local enrichement in kidney samples of mice treated with these three different compounds. Here the internal standard is required to allow intercomparisons between different individual mouse tissues.

At the end of the lecture future trends will be discussed for elemental microscopy. It will be shown that the versatility can still be improved by using laser ablation cells with higher local resolution and faster wash out time. Concerning future applications more and more metal tagged antibodies are applied in highly multiplexed immunoimaging simultaneously. From this point of view the elemental microscope can provide new analytical insights into the complex cell machinery to study a disease where it started: in cells and organs. However, LA-ICP-MS is only one tool in the tool box of multimodal spectroscopies which need to be combined in elemental and molecular microscope to study very complex biological systems. Only the combination of many spectroscopies will provide complementing informations about the inorganic and molecular composition of our sample and analyte. It looks like a dream, but we are on the best way to make it happen!

BI-IL: BIOIMAGING - INVITED LECTURES

Time: Thursday, 23/Feb/2017: 2:20pm - 2:40pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Andreas Limbeck

Session Chair: Luca Bamonti

2:20pm - 2:40pm

BI-IL: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Elemental imaging, image degradation, spatial resolution and blur, periodic gratings, convolution procedures

Image metrics for retrieval of lateral resolution and angular blur in 2D LA-ICP-MS

Johannes Teun van Elteren[1], Andrei Izmer[2], Vid Simon Šelih[1], Frank Vanhaecke[2]

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LA-ICP-MS is a well-established microanalytical technique for 2D elemental imaging of samples from biomedical, geological, archaeological, etc. origin. For proper elemental quantification and visualization of features in LA-ICP-MS maps one needs to be aware of image degradation via blur, in the form of “halo effects” (due to the physical size of the laser beam) and “smearing effects” (evoked by poor cell washout and transfer of LA generated particles), and noise (for real-world situations mostly related to flicker noise). To quantify image degradation, ablation targets with periodic gratings are required for the construction of a modulation transfer function (MTF) and subsequent determination of the lateral resolution as a function of image noise and contrast.[1]

Since ablation targets with suitable matrix composition are not readily available, computer-generated periodic gratings were virtually ablated via a computational process based on a two-step convolution procedure using empirical/experimental input data. This experimental-modeling procedure simulates LA-ICP-MS imaging based on two consecutive processes, viz. LA sampling (via ablation crater profiles [ACPs]) and aerosol washout / transfer (via single pulse responses [SPRs]).[2] We will demonstrate that by random selection of experimental SPRs from a large database for each individual pulse during the simulation, the convolution procedure simulates an accurate elemental image map of the periodic gratings with realistic noise. In this way indirect retrieval of the experimental lateral resolution is facilitated without performing actual line scanning on periodic gratings.

Although lateral resolution is normally used as a quality-criterion for imaging, we will show that linear artifacts with an angular aspect to the line scan direction may have a different spatial resolution, depending on the blur introduced as a result of “smearing effects” by the LA cell/ICP-MS interface. Via the computational approach described above, using a radial resolution target (Siemens star), we were able to visualize this angular resolution dependency. The latest generation of “ultrafast” LA cells, with FW0.01M values lower than 10 ms, minimizes “smearing effects” and as a result, the resolution becomes practically independent of the angular aspect between line scan and artifact, even for very fast scanning.

1. M. Senoner, T. Wirth and W.E.S. Unger, J. Anal. At. Spectrom. 25 (2010) 1440.

2. J.T. van Elteren, A. Izmer, V.S. Šelih and F. Vanhaecke, Anal. Chem. 88 (2016) 7413.

3. J.T. van Elteren and F. Vanhaecke, J. Anal. At. Spectrom. 31 (2016) 1998.

BI-OL 1: BIOIMAGING - GENERAL SESSION 1

Time: Thursday, 23/Feb/2017: 2:40pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Andreas Limbeck

Session Chair: Luca Bamonti

2:40pm - 2:50pm

BI-OL 1: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics, Nanomaterials

Keywords: Gold nanoclusters, Imaging, LA-ICP-MS, Metallothionein, Immunoassay

Quantitative imaging of potential protein biomarkers in oral cancer tissues with LA-ICP-MS using bioconjugated gold nanoclusters

María Cruz-Alonso[1], Beatriz Fernandez[1], Aurora Astudillo[2], Juan Carlos de Vicente[3], Rosario Pereiro[1], Alfredo Sanz-Medel[1]

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ICP–MS is being used in life sciences for trace element determination, enhancing the understanding of the role of proteins in biological systems. The analytical capabilities of ICP–MS are extended by the use of laser ablation (LA) for direct probing of solid samples. Two of the most interesting features of LA-ICP-MS are its good sensitivity and lateral resolution, allowing the elemental direct mapping of the sample surface. The combination of immunoassays (based on the specific binding of antibodies with their corresponding antigens) with LA-ICP-MS can facilitate multiparametric analyses through proper elemental tagging, allowing the mapping of proteins in biological tissues.

The use of metal nanoclusters (NCs) as elemental tags will provide signal amplification. As compared to polymeric tags, its ratio “number of metal atoms/size” is very high because they do not contain carbon or other nonmetals, resulting in a potential advantageous strategy to determine antigen distributions. In a first approach, AuNCs has been investigated in our experiments. Metallothionein (MT) distribution is known for healthy and cancerous oral tissues, so it was selected as model to validate the proposed methodology.

- **Methods**

Our synthesized AuNCs have a particle size of 2.7 nm and 580 atoms per NC [1]. We bioconjugated the AuNCs with an Anti-MT antibody and the immunoassay in the tissue section (5 microns thick) was developed. After the immunoassay protocol, detection and imaging was carried out by LA-ICP-MS and by fluorescence (confocal microscope). Studies were performed for tumor and adjacent control regions from the same patient. Calibration for LA-ICP-MS was performed with spiked gelatin standards.

- **Results**

Once the immunoassay was optimized, the MT distribution was successfully obtained by measuring the Au signal (observed background signal was negligible); the imaging of other metals in the tissues (like zinc and copper) was simultaneously carried out. The image patterns in control tissues and tumor regions were in agreement with conventional immunohistochemistry. The validation of our quantitative methodology was achieved by results comparison with HPLC-ICP-MS.

- **Conclusions**

A new and reliable analytical procedure with advantageous features for determination of MT in tissues using bioconjugated AuNCs and LA-ICP-MS has been developed. The methodology can be extended for multiplexing using different metal NCs.

- **References**

M. Cruz-Alonso, L. Trapiella-Alfonso, J.M. Costa, R. Pereiro, A. Sanz-Medel, Biosensors and Bioelectronics, 77 (2016) 1055-1061

2:50pm - 3:00pm

BI-OL 1: 2

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Laser ablation, high resolution imaging, single cell

Laser ablation with high speed and high spatial resolution: emerging applications in biological imaging

Amy J Managh, Tharwat Abduljabbar, Helen J Reid, Barry L Sharp

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Laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) is experiencing growing use for elemental mapping, most notably of biological targets. Novel instrumental approaches are facilitating increasingly faster and higher resolution imaging, enabling new opportunities that could open up LA-ICP-MS to a wider audience. Recent developments regarding fast washout, high spatial resolution and viewing optics, have been integrated into a new laser ablation imaging platform – the NWR image, which was specifically designed for rapid, high resolution imaging.

Here, we have applied the above technology for two related applications that benefit from very high spatial resolution: sub-cellular scale imaging of individual cells and imaging of small structural features in retina tissue. Fast data acquisition and appropriate data processing approaches are required to handle the wealth of information produced and to ensure that image resolution is retained. Issues around data acquisition and processing of fast transient signals for high resolution imaging will be discussed.

3:00pm - 3:10pm

BI-OL 1: 3

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics
Keywords: Wilson´s disease, copper, chelation therapy, bioimaging, LA-ICP-MS

Elemental bioimaging for the investigation of Wilson´s disease by means of LA-ICP-MS

Oliver Hachmöller[1], Andree Zibert[2], Hans Zischka[3], Michael Sperling[1,4], Hartmut H.-J. Schmidt[2], Uwe Karst[1]

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Wilson´s disease (WD) is a rare genetic disorder of the copper metabolism, causing the accumulation of copper in different organs, including liver, central nervous system and cornea. This way, WD initiates manifold hepatic, neurological or psychiatric symptoms. In the contemporary medicine, chelation therapy using D-penicillamine (DPA) is applied to remove excess copper from the organism of WD patients. To learn about the spatial distribution of various metals in the liver following chelation therapy, liver samples from LEC rats, an animal model for WD, as well as from WD patients were investigated by laser ablationinductively coupled plasmamass spectrometry (LAICPMS).

Within this work, LAICPMS was applied to study the distribution of copper, iron, and zinc in rat and human liver samples. The analysis by LAICPMS was performed with a 213 nm Nd:YAG laser using a spatial resolution of 10 µm and a scan rate of 20 µm/s. In a next step, copper, iron, and zinc were quantified by LAICPMS using homemade matrix-matched standards made of gelatine. Results revealed an influence of the DPA-treatment on the copper distribution within the liver samples and indicated a wash-out of copper in proximity to blood vessels.

The presented LAICPMS method provides a valuable tool for the investigation of the elemental distribution in liver tissue in comparison to histological staining. Methods like rhodanine staining, which is used for the visualization of the copper distribution, suffer from disadvantages like a low sensitivity in contrast to LAICPMS. Therefore, the presented LAICPMS method has the potential to become a diagnostic tool. Additionally, the efficacy of further novel chelation therapies for the treatment of WD can be evaluated by means of LAICPMS. These results may contribute to a better understanding of the chelation effect in the treatment of WD.

3:10pm - 3:20pm

BI-OL 1: 4

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics
Keywords: LA-ICP-MS, imaging, tumor spheroids, metal-based anticancer drugs

High resolution LA-ICP-MS imaging in three dimensional tumor spheroids

Sarah Theiner[1], Stijn Van Malderen[2], Thibaut Van Acker[2], Anton Legin[3], Michael Jakupec[3], Bernhard Keppler[3], Frank Vanhaecke[2], Gunda Koellensperger[1]

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Three dimensional multicellular tumor models are increasingly used as bridge between conventional monolayer cell culture systems and animal models in preclinical metal-based anticancer drug development. Depending on their size, tumor spheroids mimic the complex tumor microenvironment in terms of pathophysiological gradients and develop different regions: an actively proliferating exterior layer, a hypoxic interior and a necrotic core. Laser ablation (LA) hyphenated to inductively coupled plasma-mass spectrometry (ICP-MS) has already proven to be an optimal technique to assess metal-based drug uptake into the heterogeneous structures of tumor spheroids.[1,2] Probing the lateral platinum distribution within these tumor models allows visualizing the penetration depth and targeting of platinum-based complexes and could be used for screening drug-tumor penetration in preclinical drug development.

In the here presented study, colon cancer spheroids with various diameters were used to model different spheroid environments. The necrotic core was visualized by propidium iodide staining and tumor spheroids were treated with a platinum-based anticancer drug. An LA-ICP-MS setup was developed to investigate the platinum accumulation and characterize the tumor spheroids with different environments and degree of hypoxia and size of necrotic core at high spatial resolution.

[1] S. Theiner, E. Schreiber-Brynzak, M. Jakupec, M. Galanski, G. Koellensperger, B. K. Keppler, *Metallomics*, 2016, **8**, 398-402

[2] G. Gransbury, P. Kappen, C. Glover, J. Hughes, A. Levina, P. Lay, I. Musgrave, H. Harris, *Metallomics*, 2016, **8**, 762-773

3:20pm - 3:30pm

BI-OL 1: 5

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Bioimaging, Plants, LA-ICP-MS, LA-ICP-OES

Elemental Bioimaging in Plant Tissue Sections: Techniques for Overcoming Interferences and Reducing High Background Concentrations

Georgina Madeleine Thyssen[1], Michael Holtkamp[1], Michael Sperling[1,2], Uwe Karst[1]
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While sodium is an essential element for most animals (and humans), for plants, higher concentrations can be extremely toxic. Therefore, a detailed knowledge of the sodium distribution within plants and a comparison between salt sensitive and salt tolerant species may provide valuable information about salt resistance mechanisms. This could lead to the development of salt resistant crops with the ability to grow in the massively increasing salinized areas which are lost for agriculture right now.

Unfortunately, discovering the sodium distribution can be quite challenging from the analytical point of view as the ubiquitous appearance of sodium naturally leads to high background values. Additionally, some plant samples of interest (e.g., root tips) are of very small dimensions, demanding high spatial resolution of potential imaging techniques. As this requirement also leads to a required high sensitivity of the detection technique and as quantification opportunity is necessary, ICP based laser ablation coupling is the method of choice. Similar demands apply to other important elements in plant organisms such as calcium, potassium or iron. However, for ICP-MS, these elements also suffer from isobaric and polyatomic interferences which additionally complicate the analysis.

In this presentation, different approaches for overcoming these challenges are shown. The sodium distribution in *Arabidopsis thaliana* root tip thin sections was visualised using optimized preparation methods for low background equivalent concentrations. Due to their small diameter of only ~80 µm, an oversampling laser ablation approach was deployed, leading to a resolution of 2 µm. For highest sensitivities, a sector-field mass spectrometer under cold plasma conditions was used. Moreover, the calcium, sodium and potassium distribution in tobacco petiole and tobacco stem thin sections was investigated using LA-ICP-OES coupling to circumvent typical Ar based interferences existing in ICP-MS. Although LA-ICP-OES is not a common tool for bioimaging yet, the method proved to offer good sensitivities and a low contamination risk especially for alkali- and earth alkali elements, also allowing quantification by matrix-matched standards. In a second approach, the calcium distribution was investigated by LA-ICP-MS with an increased chemical resolution by selective mass shift reactions, enabling the screening of other elements suffering from interferences including iron, phosphorus and sulphur.

Overall, different possibilities of overcoming the special challenges of selected elements essential for plant bioimaging will be presented and compared.

3:30pm - 3:40pm

BI-OL 1: 6

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: cisplatin bioaccumulation, cisplatin induced ototoxicity, cisplatin

Characterizing cisplatin induced ototoxicity using ICP-MS and laser ablation ICP-MS

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Cisplatin is a platinum metal based chemotherapy drug used in the treatment of a variety of cancers. Cisplatin treatment has several side effects including peripheral neuropathy, nephrotoxicity, and ototoxicity. Hearing loss occurs in a significant proportion of patients undergoing cisplatin therapy. Cisplatin is toxic to several cell types in the inner ear, including sensory hair cells and supporting cells. Since uptake and clearance of cisplatin from the inner ear are poorly understood, we developed a mouse model of cisplatin ototoxicity to study repeated cycles of cisplatin administration followed by intervals of recovery, reminiscent of clinical cisplatin administration. Cisplatin uptake and clearance from the cochlea and other tissues were characterized in this mouse model using traditional ICP-MS. Unlike other analyzed organs, the cochlea abnormally accumulated cisplatin and displayed no removal of cisplatin during any point in the experiment. Our observations in mice were further corroborated by analyzing inner ears of patients treated with cisplatin. Increased levels of cisplatin were observed in those patient samples; however, the location(s) of cisplatin accumulation in the inner ear remain unknown. Molecular biology techniques have been unsuccessful in characterizing the localization of cisplatin in the inner ear. We utilized laser ablation ICP-MS to characterize the localization of platinum in these samples. High resolution laser ablation scans were performed on human inner ear tissue sections using the platinum 195 isotope to determine cisplatin localization. Calcium 43 served as the background isotope to control for drift. The images were normalized and merged using the Iolite software. In cisplatin-treated patients, levels of platinum accumulated in several areas of the inner ear. No platinum was observed in control specimens, which were obtained from patients that had not received any form of platinum-based therapy. By using traditional ICP-MS and laser ablation ICP-MS, we have determined that cisplatin clearance from the cochlea is inefficient, resulting in the accumulation of cisplatin in the inner ear. These technologies have given new insight into the mechanisms of cisplatin induced ototoxicity. Future studies will allow for the development of new therapies to prevent accumulation and ototoxicity.

BI-OL 2: BIOIMAGING - GENERAL SESSION 2

Time: Thursday, 23/Feb/2017: 5:30pm - 6:50pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Andreas Limbeck

Session Chair: Luca Bamonti

5:30pm - 5:40pm

BI-OL 2: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: laser ablation, bioimaging, human brain, silver

Quantitative Bioimaging by LA-ICP-MS for Studying the Migration of Silver from Silver-coated Endoprostheses

Michael Sperling[1,2], Mandy Großgarten[1], Ann-Christin Niehoff[1], Astrid Jeibmann[3], Werner Paulus[3], Uwe Karst[1]

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Osseous defects, which result from the removal of a tumor or metastasis, are reconstructed with mega-endoprostheses. Especially in case of oncological patients, post-operative infection rates of up to 35% occur, often followed by revision surgery or, in the worst case, by amputation of affected extremities. To circumvent bacterial infection, silver is used as implant coating due to its antimicrobial properties. However, besides killing germs, silver also affects human cells when exceeding a cytotoxic concentration level. Since information about the fate and a possible accumulation of the released silver in the organism is limited, our present work focusses on laser ablation-based elemental bioimaging of brain as possible target organ of patients with silver-coated endoprostheses.

In detail, thin brain sections of a patient with three silver-coated endoprostheses (total Ag introduction of 2.9 g) are investigated. Quantification of silver in five brain areas, including cerebellum, medulla oblongata and basal ganglia, is performed using matrix-matched standards, revealing a hundredfold increased silver concentration compared to native brain tissue of patients of the same age and sex. Additionally, high resolution LA-ICP-MS with a spot size of 4 µm is performed to allocate the silver deposits to relevant cell types. Therefore, an immunohistochemical stain with a gold-labelled secondary antibody is implemented. Overlays of the elemental distribution images of both ^{107}Ag and ^{197}Au enable the evaluation of the correlation of silver signals to marked cell type. Besides an accumulation in endothelial cells of blood vessels, silver can be co-localized to neurons and glial cells, demonstrating its ability to cross the blood-brain-barrier. Thus, elemental bioimaging by means of LA-ICP-MS empowers to obtain an improved understanding of transport, distribution, and deposition of silver in biological tissues.

5:40pm - 5:50pm

BI-OL 2: 2

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: laser ablation, imaging, elemental, molecular, biological samples

Bioimaging of Zn and MMP-11 in Breast Cancer Tissues by LA-ICP-MS and MALDI-IMS

Raquel Gonzalez de Vega[1], Maria Luisa Fernandez-Sanchez[1], Noemi Eiró[2], Francisco Vizoso[2], Alfredo Sanz-Medel[1], Uwe Karst[3]

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The matrix metalloproteinases (MMPs) are a family of zinc-dependent endopeptidases. The main functions of this metalloproteinases are the degradation of the stromal connective tissue and basement membrane components. Recent data from model systems suggest that MMPs are involved in breast cancer (BC) initiation, invasion and metastasis. Particularly, MMP-11 (Stromelysin-3) is expressed in stromal fibroblasts adjacent to epithelial tumor cells, and high levels of this metalloproteinase were associated with tumor progression and poor prognosis of BC. Consequently, MMP-11 involved in these processes can be a candidate to be identified as new prognostic biomarker in BC.

On the other hand, concentrations of trace elements naturally present in breast tissues have been studied as a new tool for prevention, diagnosis and treatment of breast cancer. Elements such as Ca, Fe, Cu and Zn are believed to play key roles since they are responsible for a great number of metabolic and biological processes. Due to increased metabolism rates they furthermore appear in altered concentrations in cancer tissues.

Bioimaging analytical techniques, based in LA-MS, have been rapidly growing in biology and medicine for studies of biological systems to provide information of biomolecules (such as proteins, metabolites, and lipids) and metals with lateral resolution at the micrometer scale.

In particular, elemental mass spectrometry based analytical methods (e.g. laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS) have been developed for bioimaging of essential trace metals (Ca, Fe, Cu and Zn) and no metals (S, P and Se) in biological tissues.

Moreover, combinations of immunohistochemistry assays with LA-ICP-MS technique and/or matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) have been widely applied for imaging and mapping of expression of protein biomarkers implicated in breast cancer with high sensitivity and high local resolution.

In this particular study, the application of Matrix Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry Imaging (MALDI-MSI) was carried out to investigate the actual distribution of MMP-11 in breast cancer tissues in order to show a possible correlation and to reveal its role in cancer progression. Additionally, human breast tissue samples were also analyzed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), to provide additional information about the elemental distribution of Zn which is associated with MMPs as well as other important metabolic processes.

5:50pm - 6:00pm

BI-OL 2: 3

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Gadolinium-based contrast agents, gadolinium deposition, human brain, bioimaging, quantification

Spatially resolved quantification of gadolinium in human brain thin sections by means of LA-ICP-MS after administration of gadolinium-based contrast agents

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Due to its paramagnetic properties resulting from seven unpaired f-electrons, Gd is frequently used in magnetic resonance imaging (MRI). It increases the relaxation rate of surrounding protons, thus enhancing the contrast between different tissues in the same MR image. In regard to the acute toxicity of free Gd^{3+}, the contrast agent (CA) cannot be applied as free ion. Therefore, polyaminocarboxylates like diethylenetriaminepentaacetate (DTPA) are used to create thermodynamically stable linear or macrocyclic complexes with Gd^{3+}. The highly water soluble CAs are known to be excreted fast and unmetabolized, mostly via the kidneys. Nevertheless, recent studies showed that Gd persists not only in animal but also in human brain. Even individuals without renal dysfunction reveal trace amounts of Gd remaining in the organism. In this context, Kanda et al. quantified the total Gd content in globus pallidus and dentate nucleus of patients without renal dysfunction treated with Gd-based CAs (GBCA).[1]

To reveal the distribution of Gd within the brain of patients after GBCA administration, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) as a powerful tool for the localization and quantification of trace amounts of Gd was applied in this study. Cryosections of different brain regions with a thickness of 10 µm were ablated line by line using a 213 nm Nd:YAG-laser with a spot size of 50 µm and a scan rate of 100 $\mu m \cdot s^{-1}$. For quantification of Gd, matrix-matched standards based on gelatin were prepared. The presented LAICPMS method offers a limit of quantification (LOQ) for Gd of 7 $ng \cdot g^{1}$. In addition to basal ganglia and dentate nucleus, Gd could be detected in frontal lobe cortex and pons as well, even two years after the last administration of a linear GBCA. Thus, this study contributes to a better understanding of Gd deposition in different brain regions which is currently under extensive discussion.

[1]Kanda, T. et al., Radiology, 2015, 276, 228-232.

6:00pm - 6:10pm

BI-OL 2: 4

Topics: Elemental analysis

Keywords: blood analysis; laser ablation; solid sampling; ICP-MS

New strategies for analysis of biological samples via ICP-MS

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The analysis of biological fluids, such as blood or urine, entrains a certain number of problems in all steps of the analytical process. In this regard, collection and preservation of such samples as well as transportation to the analytical lab is especially problematic, requiring a considerable amount of resources. The deposition of biological fluids onto clinical filter paper, giving rise to the so-called Dried Matrix Spot (DMS) shows important advantages from a logistic point of view.[1-3] However, development of methods that permit the direct analysis of these specimens is far from straightforward. In this presentation, the different characteristics of Dried Urine Spots (DUS) and Dried Blood Spots (DBS) will be discussed in detail, with the aim of developing methodologies that permit the elemental and isotopic analysis of both types of samples via ICP-MS. The potential of new types of available DMS specimens and the suitability of atomic techniques for their direct analysis, including approaches to mitigate spectral and non-spectral interferences will also be discussed.

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Acknowledgements

MR acknowledges the funding from CTQ2015-64684-P (MINECO/FEDER) and from the Aragón Government (Fondo Social Europeo). FV acknowledges funding from the Ghent University Special Research Fund (BOF-UGent). Águeda C. would like to thank the Vice-Presidency for Research of the University of Alicante (ref. UAFPU2015-5990) and the Generalitat Valenciana, Spain (ref. ACIF/2016/042)for the pre-doctoral grants.

6:10pm - 6:20pm

BI-OL 2: 5

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-MS, single cell analysis, single spot ablation, bioimaging

Quantitative LA-ICP-MS of single cells: Comparison of single spot ablation and imaging

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LA-ICP-MS finds widespread use in the analysis of biological samples and its importance as an analysis method is still increasing. Often tissues or single cells are ablated in imaging mode on glass slides [1], but the analysis time increases by reducing the spot size of the laser. Additionally with increased lateral resolution a loss in sensitivity is inherently connected and this holds true in particular for single cell analysis in imaging mode. However, if only the composition of elements in a single cell needs to be measured, complete ablation of cells by single shots looks promising. This approach was already discussed by Managh et al. [2] and will be discussed in more detail in this presentation. It is the aim of this study to develop a calibration strategy for single cell analysis based on the *total consumption* concept. It will be shown that this concept provides quantitative results at single cell level, if the target material is ablated. We compare two different laser spot sizes, 30 µm and 110 µm. The smaller spot size of 30 µm will be used for imaging and the larger spot size of 110 µm will be used for the targeted ablation of complete single cells. Cells were stained by two novel cell dyes, mDOTA-Tb (CheMatech, Dijon, France), which binds to free thiol groups of proteins, and Ir-DNA intercalator (Maxpar®, Fluidigm, San Francisco, USA), which stains DNA quantitatively. Finally, quantification of Ir and Tb will be performed by matrix matching calibration, following the approach of Drescher et al.[1], i.e. spotting of a dilution series of Ir and Tb standards on nitrocellulose membrane. Results obtained so far show a surprisingly good correlation between imaging and single spot ablation, indicating that the total consumption theory may serve as an acceptable assumption.

1. Drescher, D., et al., *Quantitative imaging of gold and silver nanoparticles in single eukaryotic cells by laser ablation ICP-MS.* Analytical Chemistry, 2012. **84**(22): p. 9684-9688.

2. Managh, A.J., et al., *Single Cell Tracking of Gadolinium Labeled CD4+ T Cells by Laser Ablation Inductively Coupled Plasma Mass Spectrometry.* Analytical Chemistry, 2013. **85**(22): p. 10627-10634.

6:20pm - 6:30pm

BI-OL 2: 6

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: elemental distribution, LA-ICP-MS, EDX, confocal microscopy, phytoremediation

Application of LA-ICP-MS, EDX and confocal microscopy for imaging and quantifying Cd, Cu, Zn and Pb in tissues of pea (Pissum sativum L.)

Anetta Hanć[1], Arleta Małecka[2], Agnieszka Kutrowska[2], Danuta Barałkiewicz[1]

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Elements can be divided into: indispensable (essential) for the proper functioning of the plant cell or unnecessary - not involved in cellular metabolism and toxic even in small quantities (e.g. Cd, Pb, Hg, Al). Essential elements also induce toxicity symptoms if they are present in excess. A much larger portion of metals after uptake by plants is accumulated in the roots. Certain metals are transported then from the roots to the shoots by xylem.

Analysis of elements in the plant material, a number of experiments were performed using analytical methods (ICP-MS, LA-ICP-MS, EDX) and confocal microscopy technique. Qualitative and quantitative methods were developed for Cu, Pb, Cu and Zn mapping and quantification in root of pea *Pisum sativum L*. Plants were cultivated hydroponically in the Hoagland medium with the addition of 50 µM of $CdCl_2$, $Pb(NO_3)_2$, $CuSO_4$, or $ZnSO_4$. After 48h, parts of roots were cut and analyzed [1].

LA-ICP-MS was used for in vivo quantitative imaging of the distribution of metals in thin sections of root tissues. Calibration curve was obtained using standard addition method to matrix matched material: NIST SRM 1515 Apple Leaves spiked with standard solution and selection of sulfur isotope ^{34}S as an internal standard. EDX was used in order to confirm results obtained by LA-ICP-MS and identify the exact localization of metal deposits in root tissue. In the electron-microscopic photographs we observed deposits of metals in the cell wall, cell membrane, vacuoles, cytoplasm and organelles, such as: mitochondria and peroxisomes. Formation and localization of O_2^- and H_2O_2 in cross-sections of root tips was confirmed by confocal microscopy. The presence of metals induced ROS (reactive oxygen species: O_2^-, H_2O_2) production in areas corresponding to patterns of metals accumulation [2].

By using different research techniques the estimated capacity of pea plants to absorb, transport and accumulate the trace metals to the aboveground parts of plants and the possibility of their potential use in the phytoremediation was assessed.

[1] A. Hanć, A. Piechalak, B. Tomaszewska, D. Barałkiewicz, Int. J Mass Spectrom. 363, 2014, 16–22.

[2] A. Hanć, A. Małecka, A. Kutrowska, A. Bagniewska-Zadworna, B. Tomaszewska, D. Barałkiewicz, Microchem. J 128, 2016, 305–311.

BI-OL 2: 7

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: laser ablation, inductively coupled plasma mass spectrometry, elemental imaging, biological tissues, geological materials

Laser ablation inductively coupled plasma mass spectrometry in elemental imaging of inorganic and biological materials

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LA-ICP-MS was used for study of lateral distribution of elements in biological and geological materials with the aim to provide information necessary for elucidation of processes in tissues and rocks. Besides, glass artifacts were characterized.

Quadrupole (Agilent 7500 CE, Agilent Technologies) and sector field (ELEMENT 2, ThermoFisher Scientific) ICP-MS instruments with Nd:YAG (213 nm, UP 213, New Wave Research) and ArF* (193 nm, Analyte G2, Teledyne CETAC Technologies, Photon Machines) lasers used in this work offer adequate sensitivity and sufficient spatial resolution after thorough optimisation.

Spatially resolved LA-ICP-MS analysis of biological materials, such as tumours, tissues and plants provides lateral distribution of essential and toxic elements. Analysis of tissues and cultivated cells is performed for monitoring the penetration of candidate anti-cancer drugs into cancer cells. Local spot analysis as well as mapping of selected areas of geological materials and glass artifacts show distribution of main constituents, trace elements and provide imaging of different phases and minerals in rocks. Quantification of elemental maps is performed.

New, original results were obtained in domain of biological tissues and inorganic materials.

Acknowledgement: The results of this research have been acquired within CEITEC 2020 (LQ1601) project with financial contribution made by the Ministry of Education, Youths and Sports of the Czech Republic within special support paid from the National Programme for Sustainability II funds.

APP-PL: APPLICATIONS AND FUTURE TRENDS - PLENARY LECTURE

Time: Friday, 24/Feb/2017: 8:30am - 9:00am
Location: ARLBERG-well.com NORTH HALL
Session Chair: Steven James Ray
Session Chair: Daniel Pröfrock

8:30am - 9:00am

APP-PL: 1

Topics: Sample introduction and sample preparation, Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Glow discharge mass spectormetry, Coupling techniques (chromatography, FFF, ETV, others), Metallomics, Nanomaterials, Plasma source fundamentals, instrumentation and mechanisms
Keywords: future, plasmas, instrumentation, optical spectrometry, mass spectrometry

A Brief Gaze into the Plasma Spectrochemistry Crystal Ball

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There are five common ways to predict the future; all have proponents and opponents, all boast examples of success, and all have been utilized extensively. All but the last will be used here to assess where plasma spectrochemistry might head over the next several years. The first of these approaches is to extrapolate past trends into the future; as Confucius wrote, “Study the past if you would define the future.” Clearly, this approach is conservative and likely to be at least somewhat successful, although it is a bit like trying to drive a car by looking in the rearview mirror; unexpected deviations can nullify any projections. The second is a bit broader and a bit less prone to error: study “megatrends” in social, scientific, and economic issues and project how they will affect a particular area (plasma spectrochemistry in the present situation). The third is similar but more tightly focused; examine peripheral areas (here, plasma physics, technology, and applications; novel mass and optical spectrometric systems; emerging detectors) and see how they will or might impact plasma spectrochemistry. A fourth method is to gauge which weaknesses of a system are most troublesome and to devise or adopt alternatives that overcome the weaknesses. The fifth approach is the most common and the one treasured by politicians: make vague guesses and, when the future arrives, claim to have foreseen it all along.

Perhaps a good starting point for our discussion is to look back 100 years and use it as a backdrop to the present. In 1917, the world was deeply embroiled in WWI and nations were being born, torn apart, and redefined. However, there were far more promising and positive events. In that year, Albert Einstein published his paper defining and explaining stimulated emission, the basis for all laser action. Also, John Fenn, inventor of electrospray ionization, was born, as was Arthur C. Clarke, science fiction writer and inventor of the geostationary communications satellite and the “space elevator”, the latter still to be reduced to practice. So, at least for now, this brings us full circle, for as Clarke once expressed in his three “laws”:

1. When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong.

2. The only way of discovering the limits of the possible is to venture a little way past them into the impossible [*i.e. consider science fiction*].

3. Any sufficiently advanced technology is indistinguishable from magic.

Let us then venture from the probable, to the possible, and perhaps approach what might be the science fiction of plasma spectrochemistry…

APP-IL: APPLICATIONS AND FUTURE TRENDS - INVITED LECTURES

Time: Friday, 24/Feb/2017: 9:00am - 9:40am
Location: ARLBERG-well.com NORTH HALL
Session Chair: Steven James Ray
Session Chair: Daniel Pröfrock

9:00am - 9:20am

APP-IL: 1

Topics: Isotope ratio analysis, Environmental sciences, Metrology in chemistry
Keywords: Hg, speciation, isotops

Hg fractionation, speciation, fish: New tools to unravel the global cycling of Hg

Olivier F.X. Donard[1], David Amouroux[1], Sylvain Berail[1], Emmanuel Tessier[1], Julien Barre[1], Mathilde Monperrus[1], Zoyne Pedrero[1], Russel D. Day[2]

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The hyphenation of chromatography techniques to ICP/MS have allowed to result in major advances in the global understanding of trace elements cycling. Tremendous progress have been made over the last 20 years with the implementation of speciation analysis using hyphenated chromatography techniques to quadrupoles ICP/MS. This has led to the implementation of the use of isotopically labelled approaches in the analytical scheme and have brought tremendous progress to the field allowing to unravel major artifacts during the sample preparation and hence questioning global environmental results. The development of plasma based multicollector has allowed to use the flexibility of the instrument to evidence for the occurrence of different isotopic signature of Hg in the environment. Mass dependent and mass independent fractionation signatures of Hg have been related to sources and process and have then allow to shed new light on the global Hg cycling. Further progresses and questions appear now since we can look in greater detail at the isotopic fractionation of Hg species (methymercury, ethylmercury, and inorganic mercury) in the samples of fish samples for example. Their isotopic signatures are significantly different and this raises then fundamental questions with regards to the fate and transformation of Hg during its global cycling and assimilation into food webs. In order to fully assess these questions, we need to fully control the full analytical chain to inform new global Hg cycling views using sound and defensible metrology. Using species specific isotopic signatures is a promising new technique that will enhances the array of environmental descriptors available. But then, there are important questions related to precision and accuracy of the isotopic determination of these individual species during the whole analytical chain. We will review all of the critical steps of the analytical chain related to Hg determination in fish to evaluate the major advances and areas that need improvement so that we can attain a better understanding of the global cycling of Hg. Results will include new data on NIST SRM 1947 Lake Michigan Fish Tissue and other potential fish RMs, and highlight the importance for additional reference materials in this new domain.

9:20am - 9:40am

APP-IL: 2

Topics: Elemental analysis
Keywords: arsenic, fluorine

Traditional elemental speciation and newcomers

Jörg Feldmann, Eva Krupp, Johannes Kopp, Nor Laili A. Jamari, Andrea Raab
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Speciation analysis is the key to describe analysis in the environment and in biology.

This lecture will revisit speciation analysis by using HPLC-ICP-MS/ESI-MS for traditional elements. The focus will be on the analysis of arsenic in the marine environment especially the accumulation of arsenic in the top preditors such as pilot whales.

The second part will focus on the development of a speciation method to determine organofluorine species using HPLC-ICP-MS.

The details will be given at the lecture....

APP-OL 1: APPLICATIONS AND FUTURE TRENDS - GENERAL SESSION 1

Time: Friday, 24/Feb/2017: 9:40am - 10:50am

Location: ARLBERG-well.com NORTH HALL

Session Chair: Steven James Ray

Session Chair: Daniel Pröfrock

9:40am - 9:50am

APP-OL 1: 1

Topics: Isotope ratio analysis

Keywords: Nuclear, Forensics, Uranium, Plutonium, isotopes

Advances in Nuclear Forensics

M. Paul Field[1], Kayron N. Tevepaugh[2], Brian W. Ticknor[2], Hwan Kim[1], Shalina C. Bottorff[2], Cole R. Hexel[2]

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Implementing a defensible nuclear forensics program requires overcoming the challenges of measuring precise and accurate U and Pu isotope ratios in very small sample quantities. Here we evaluate the performance of, 1) a fully automated chromatography system, 2) a syringe loading and injection system, and 3) an aerosol desolvation system as a complete solution for the preparation and analysis of nuclear forensic samples.

The fully automated chromatography (prep*FAST*-MC; ESI, Omaha, USA), is a low pressure chromatography system that isolates elements of interest from the sample matrix and collects multiple discrete eluent fractions for precise isotopic analysis. In a dual column configuration sample is loaded unto two columns (C1 and C2), then each is washed of matrix before eluting U from C1 and Pu from C2. Automating U and Pu separation provides high recoveries, no carryover (undetectable), low blanks and reproducible extractions.

The fully automated syringe loading and injection system (micro*FAST*-MC; ESI, Omaha, USA) is a dual loop injection system that syringe rinses and loads sample into one loop, while syringe injecting sample from the other loop to a µFlow concentric nebulizer. The micro*FAST*-MC is used to eliminate waste and provide total sample consumption. Software defined sample volumes and injection flow rates are set to 220 mL and 50mL/min, respectively. This provides 4 minutes of stable signal for 500 femtograms of plutonium.

The software controlled desolvation system (apex W; ESI, Omaha, USA) combines multistage Peltier-cooling and a helical EPTFE fluoropolymer membrane with full software control of gas flow rates (N2 and Ar) and temperatures (spraychamber, Peltier and membrane). The apex W is used to enhance sensitivity of U and Pu and reduce and hydride interferences that adversely affect accuracy of isotope ratios.

The final result is that accurate and precise ratios are obtained for $^{240}Pu/^{239}Pu$ on 500 femtograms of CRM (082 and 126) and for $^{234}U/^{238}U$ and $^{235}U/^{238}U$ and $^{236}U/^{238}U$ on 400 picograms of CRM (183) using a NEPTUNE *Plus* MC-ICP-MS with Jet Interface option (Thermo Scientific, Bremen, Germany)

9:50am - 10:00am

APP-OL 1: 2

Topics: Sample introduction and sample preparation

Keywords: Grid nebulizer, dual channel, online, standard addition

Dual-channel Concentric Grid Nebulizer for applying online standard addition ICP-OES

Kazumi Inagaki, Rina Matsushita, Koyo Ido, Shin-ichi Miyashita, Shin-ichiro Fujii

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Inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the useful techniques for trace element analysis in various research fields. For analyzing high matrix samples, a standard addition method benefits for canceling matrix effect in measurement. However, a conventional standard addition approach is time consuming, because individual calibration curves are required for each sample, then several mixing solutions of a sample and a standard have to be prepared for each sample. One approach for overcoming the above drawback is making an online standard addition system using a dual-nebulizing unit. Several dual-nebulizing units have been developed for utilizing online standard addition method, but these have some drawbacks in reproducibility, sensitivity, or handling.

We applied a dual-channel type concentric grid nebulizer (D-CGrid) for online standard addition. The D-CGrid has a unique structure, one nozzle with a grid screen and two independent liquid flow lines set inside the nozzle. The liquids are well-mixed in a small space just before the grid screen, because the grid acts as a dumper. The mixture of the liquids breaks-up into small droplets by passing through the grid, resulting in simultaneously and efficiently nebulizing two liquids without pre-mixing before introducing into the nebulizer. The nebulizing performance for two liquid channels are almost the same, thereby the same sensitivity in ICP-OES can be obtained with each liquid channel. We will show the performance of online standard addition with the D-CGrid by analyzing some biological reference materials.

10:00am - 10:10am

APP-OL 1: 3

Topics: Sample introduction and sample preparation

Keywords: Fruit juice, Milk, ICP OES, Sample preparation, Flow system

Application of high pressure microwave-assisted digestion flow system for juice and milk sample preparation

Thiago Linhares Marques[1], Joaquim Araújo Nóbrega[1], Helmar Wiltsche[2], Monika Winkler[2], Günter Knapp[2]

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Sample preparation is usually required for metals determination in food samples by inductively coupled plasma optical emission spectrometry (ICP OES), since matrix effect of carbon in the plasma is a main reason to obtain unreliable data. Microwave-assisted acid digestion is a well-known and widely applied technique for food sample preparation, but, it is usually performed in batch mode which may led to analytical errors due to sample handling. Flow analysis is a good approach to overcome these drawbacks, but care must be taken, since the short residence time of the sample in the irradiated zone led to lower efficiency of digestion compared batch procedures. This can be improved increasing the reactor volume as shown by Marques et al. (2016)[1]. In the literature, there are just few applications of high pressure flow systems for liquid sample digestion, such as fruit juices and milk. These samples are not easily digested in an on-line flow system, because juices are rich in sugars that promote violent reactions inside the reactor and milk is rich in fats that are not easily degraded. In the work here described, the performance of a high pressure microwave-assisted flow digestion system with large volume reactor was evaluated to digest these samples. The digestions were carried out in a coiled perfluoroalkoxy (PFA) tube reactor (13.5 mL) put inside a labmade autoclave pressurized at 40 bar. The system was operated at 500 W microwave applied power and 5.0 mL min^{-1} flow rate. Juice samples of apple and mango were successfully digested in this flow system using 3.7 mol L^{-1} HNO_3 and 0.3 mol L^{-1} HCl. The residual carbon contents (RCC) were 16 and 29% for apple and mango juices, respectively, when juice samples were diluted to a final concentration of 67% V/V. Concentrated HNO_3 (10.5 mol L^{-1}) was effectively applied for digesting milk samples and the RCCs were 23 and 25% for partially skimmed and whole milk, respectively, when milk samples were diluted to a final concentration of 25% V/V. Calcium, Fe, K, Mg, Na, P, S, Sr and Zn were determined in both types of samples and Al, Ba, B, Cu and Mn were determined in juice samples by ICP OES. According to F test the precision of the high pressure microwave-assisted digestion flow system was similar to microwave-assisted digestions performed in closed-vessels (batch mode) for most elements. Elemental contents determined in juice and milk samples digested in flow mode were in good agreement with those determined in samples digested in batch mode according to a t-test adopting a confidence interval of 95%.

Acknowledgements: The authors acknowledge the financial support given by Science without Borders and CNPq (process number 249068/2013-3 and 140474/2013-7).

[1] T.L. Marques, H. Wiltsche, H. Motter, J.A. Nóbrega, G. Knapp, J. Anal. At. Spectrom. 30 (2015) 1898–1905.

10:10am - 10:20am

APP-OL 1: 4

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-TOFMS imaging, collision/reaction cell technology

Rapid multi-elemental imaging using LA-ICP-TOFMS in combination with collision/reaction cell technology

Marcel Burger[1], Gunnar Schwarz[1], Alexander Gundlach-Graham[1], Debora Käser[1], Jerôme Käslin[1], Bodo Hattendorf[1], Daniela Rubatto[2], Detlef Günther[1]

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Laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS) is a powerful and versatile micro analytical technique that enables the determination of a given sample's local bulk composition as well as high-speed, high-resolution, multi-elemental imaging of geological and biological specimens.

Latest generation ICP-TOFMS instrumentation discussed here (*icp*TOF, TOFWERK AG Thun, Switzerland) features a collision/reaction cell upstream of the TOF mass analyzer that expands its performance capabilities. When filled with a bath gas of He, the collision cell cools the ion beam so that mass resolving powers up to $RP_{(FWHM)}$=5000 can be achieved. Additionally, operating the cell in a reaction mode with H_2 gas allows for the suppression of undesirable interferences and enhanced sensitivity for hard-to-measure isotopes such as ^{40}Ca and ^{80}Se.

Apart from providing a detailed characterization of the *icp*TOF in combination with low-dispersion, as well as high-dispersion LA-based sample introduction systems, this study specifically discusses the applicability of collision/reaction cell technology in low-dispersion LA imaging experiments. Effects of He and H_2 gas flows through the collision/reaction cell on signal structure and background intensities are carefully addressed. Abundance sensitivities and peak shapes observable in ICP-TOFMS spectra are reported and their implications for detection power and quantification capabilities are discussed. The suitability of baseline fitting approaches to overcome some of the abundance sensitivity issues are evaluated.

To demonstrate capabilities of low-dispersion LA-ICP-TOFMS in combination with collision/reaction cell technology, results of an imaging case study focusing on trace element distribution in garnet samples are presented.

10:20am - 10:30am

APP-OL 1: 5

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: Sn isotope ratios, archaeometry, cassiterite, laser ablation, MC-ICP-MS

Application of femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry (fs-LA-MC-ICP-MS) for tin isotope ratio analysis in cassiterite

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In Archaeometry isotope ratio analyses are often used for provenance studies determining the sources of raw materials used for ancient metal objects. For tracing the origin of ancient tin and bronze artefacts, tin isotopy came into focus, especially in recent years. Promising results concerning provenance studies using tin isotope ratios have already been published by multiple international research groups. All previous studies were performed by liquid analysis. That requires a time consuming sample preparation including ore reduction, dissolution and purification procedures and sample material in a double-digit milligram range. In comparison to isotope analysis in dissolved samples femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry (fs-LA-MC-ICP-MS) enables isotope ratio analyses using much less sample material with a minimum sample preparation. This would be especially important for the investigation of historical objects for provenance analysis without visual traces of sampling using laser spots of 100 µm at maximum.

In this project the applicability of fs-LA-MC-ICP-MS for tin isotope ratio analysis of cassiterite and metal objects was investigated. In-house isotope standards were defined because no certified reference materials were available. Systematical studies concerning interferences and matrix effects using solutions showed that beside Sb only high Te contents significantly influence the tin isotope ratios. This isobaric interference can partly be corrected using natural abundances of Te isotopes.

Comparisons of isotope ratios obtained for tin beads reduced from cassiterite by KCN analysed by laser ablation and after dissolution showed that tin isotope ratios can accurately be determined by fs-LA-MC-ICP-MS. Furthermore the homogeneity of tin isotope ratios in cassiterite could be proved.

Fractionation effects during reduction processes are investigated by laser ablation which enables the direct comparison of the received tin metal and the slightly soluble raw material.

By analysing as much cassiterite samples of known origin as possible, the extent of isotope variations of one ore deposit and the possibility of a differentiation of worldwide cassiterite deposits using laser ablation will be investigated in detail.

Further studies applying fs-LA-MC-ICP-MC for tin isotope analysis of bronze will also examine the potential of laser ablation for the minimal invasive investigation of objects of cultural value.

10:30am - 10:40am

APP-OL 1: 6

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: ICP-TOFMS, Laser ablation, Imaging

A 213 nm Laser Ablation System in Conjunction with ICP-TOFMS for High-Resolution, High-Speed and Multi-Elemental Imaging

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Purpose

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) imaging provides valuable insights to the elemental distribution within solid materials. Comprehensive and high lateral resolution as well as multi-elemental analyses are however compromised by laser spot sizes, pulse-to-pulse aerosol mixing and limited multi-elemental detection capabilities of most ICPMS detectors. Here, we describe a setup to address these drawbacks.

Methods

A laser ablation setup consisting of a solid state Nd:YAG-based 213 nm laser an optical system capable of focusing the laser beam to a few µm in diameter in conjunction with a low-dispersion laser ablation tube cell was coupled to an ICP-TOFMS (*icp*TOF, TOFWERK, Thun, Switzerland). For high information density data, the ICP-TOFMS was operated in high time resolved data acquisition mode, with shot-to-shot signal separation. The results were compared to an Excimer-based 193 nm LA system.

Results

The optical system provides laser spot diameters as small as 1 µm, the low-dispersion tube cell maintains a compact aerosol plug with transient signal duration below 10 ms (full width at 1% peak maximum) of single ablation events. The high-resolution, high-speed and quasi-simultaneous multi-element imaging capabilities are demonstrated by LA-ICP-TOFMS experiments on a variety of samples, including reference glass, geological samples and biological thin tissue sections.

The easier to operate solid state Nd:YAG-based 213 nm system is currently limited to a laser repetition rate of 20 Hz. However, it provides similar or equal characteristics with respect to spatial and temporal resolution as the previously described Excimer-based 193 nm system, e.g. subcellular resolution for biological thin sections.

Conclusion

The presented approach is well suited to perform LA-ICPMS imaging in various analytical applications.

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10:40am - 10:50am

APP-OL 1: 7

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-MS, ICP-OES, Litihium ion battery

INVESTIGATION OF AGED LITHIUM ION BATTERY ELECTRODES BY MEANS OF LA-ICP-MS AND ICP-OES

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Due to a lack of reliable methods for µm-scale determination of the elemental distribution in aged lithium ion battery (LIB) electrodes, a method using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is developed. The solid sample is investigated using a 193 nm ArF Excimer Laser with spot sizes ranging from 2.5-150 µm and subsequently analyzed in an ICP-MS. As the LA-ICP-MS technique is used as a bulk quantification method, the inductively coupled plasma optical emission spectroscopy technique (ICP-OES) is chosen as a reference after a microwave assisted acid digestion.

In a typical LIB system, a certain degree of performance loss is witnessed because of various componential failures. Hence, understanding the different aging processes of the cell components (e.g. cathode, anode, electrolyte etc.) is a major factor for improving e.g. cycle life, capacity, rate capability and safety of a battery system.

In this work, an investigation of the connection between solid electrolyte interphase (SEI) and lithium loss, which is attributed to the consumption via the SEI formation in the course of the first cycle, is carried out. During the lithiation of a graphite electrode, different graphite intercalation compounds (GICs) are formed based on the applied voltage. Four of these GICs are mainly investigated in this work. During the first cycle, the electrodes are initially lithiated to a certain state of charge or GIC (LiC_{30}, LiC_{18}, LiC_{12} and LiC_6), respectively. Afterwards, they got completely delithiated to maintain, theoretically, a graphite electrode with nothing but an SEI covering the particles.

The results are able to provide insights into the process of SEI formation with regard to the irreversible lithium loss which is caused by this process.

APP-OL 2: APPLICATIONS AND FUTURE TRENDS - GENERAL SESSION 2

Time: Friday, 24/Feb/2017: 11:20am - 1:30pm

Location: ARLBERG-well.com NORTH HALL

Session Chair: Steven James Ray

Session Chair: Daniel Pröfrock

11:20am - 11:30am

APP-OL 2: 1

Topics: Elemental analysis

Keywords: ID-ICP-QMS/QMS, BaF, drinking water

Measuring of BaF by ICP-QMS/QMS for Determination of F in Drinking Water

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Inductively coupled plasma mass spectrometer (ICP-MS) is a powerful instrument for elemental analysis covering most of the elements in the periodic table of the elements. However, there are few reports on the determination of fluorine, which is a monoisotopic element with ^{19}F as its stable isotope. The major reason is that fluorine has a much higher ionization energy (approximately 17.42 eV) than that of argon (approximately 15.76 eV), which indicate that the sensitivity of fluorine measurement is very low since that the ionization of fluorine is difficult and hindered by the ionization of argon. In the present work, an alternative approach was suggested for the determination of fluorine by ICP-MS.

In order to improve the sensitivity of measurement, $^{138}Ba^{136}F^+$ was selected as the measurand instead of $^{19}F^+$. Barium has a much lower ionization energy (approximately 5.2 eV) than that of argon. As the result, $^{138}Ba^+$ ions could be easily formed in the argon plasma. At the same time, neutral fluorine atoms are plenty in the argon plasma. These facts permitted the formation of $^{138}Ba^{19}F^+$ ions in the argon plasma.

The measurement of $^{138}Ba^{19}F^+$ suffers spectral interferences from $^{138}Ba^{18}O^1H^+$, $^{138}Ba^{17}O^1H_2^+$, and $^{138}Ba^{16}O^1H_3^+$. Therefore, an ICP-MS with a pair of tandem quadrupole mass spectrometer, *i.e.* ICP-QMS/QMS, was utilized for measurement. High energy collision mode with oxygen gas as the reaction gas was applied for separating the spectral interferences.

In the present work, it was found that a “mild” plasma condition with an RF power of approximately 1350 W permitted the best performance for $^{138}Ba^{19}F^+$ measurement, *i.e.* providing the highest signal/noise ratio. At the same time, high energy collision mode with a cell gas flow rate of 0.7 mL O_2 min^{-1} provided the best spectral interference separation for $^{138}Ba^{19}F^+$ measurement. The sensitivity of $^{138}Ba^{19}F^+$ measurement was in linear correlation with the concentration of barium (up to 100 mg kg^{-1}) in the sample. When the concentration of barium was over 100 mg kg^{-1}, deterioration of the formation efficiency of $^{138}Ba^{19}F^+$ was observed. The results of investigation on matrix effect showed that the sensitivity of $^{138}Ba^{19}F^+$ was affected by the concentration of cations such as Na^+ in the sample but not by that of the anions such as Cl^-.

The detection limit of fluorine with 10 mg kg^{-1} barium was 0.06 mg kg^{-1}, which permitted the precise analysis of a drinking water certified reference material. The observed value of fluorine in ERM CA 015-a was (1.36 ± 0.05) mg kg^{-1}, which agreed with the certified value (1.3 ± 0.1) mg L^{-1}, indicating the usefulness of the present approach for fluorine measurement.

11:30am - 11:40am

APP-OL 2: 2

Topics: Elemental analysis, Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-MS, fast, multi-element, imaging, isotope ratios

How can TOF contribute to LA-ICP-MS applications?

Olga Borovinskaya[1], Martin Tanner[1], Hao Wang[2], Julien Mercadier[3], Jon Woodhead[4]

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Laser ablation ICP-MS has a number of distinct advantages over traditional solution ICP-MS such as speed, smaller consumption volume and much easier sample preparation. The main reason for its popularity is, however, the ability to preserve spatial information. While the highest signal stability is aimed for solution measurements, in laser ablation isotope signal variation is often the source of valuable information. Therefore, correct registration of these varying signals is extremely important for high-quality analysis. Simultaneous mass analyzers have long been recognized as most suitable for LA-ICP-MS. However, until recently, simultaneous ICP-MS instruments had insufficient performance or were designed for specific applications, as multi-collector ICP-MS for precise isotope measurements but in a limited mass range or cytometry time-of-flight mass spectrometers (TOFMS) for the analysis of single cells labeled with rare earth elements. In 2014, TOFWERK launched an ICP-TOFMS under the brand name *icp*TOF which provides low detection limits, high acquisition speed, and medium mass resolution combined with collision/reaction cell technology for interference treatment. In this contribution we present recent developments and applications of this instrument.

Because all isotopes are registered all the time, the signal duration is no longer a limiting factor and signals of <1s, commonly generated from tiny grains and inclusions, can be accurately measured. We demonstrate the performance of the *icp*TOF in combination with low aerosol dispersion ablation cells for the fluid inclusion analysis evaluated on synthetic silica capillaries and quartz samples. In bulk analysis the ablated volume per analysis can significantly be reduced with the *icp*TOF, which is extremely valuable for precious samples. We show the application of the *icp*TOF for origin determination of colored gemstones and quantification capabilities based on a few laser shots.

Isotope ratio analysis requires very high precision and accuracy, best achievable with simultaneous mass spectrometers. Additional information on trace element composition and different isotopic systems is very valuable in the interpretation of geochronological results. In this study we evaluate the application of the *icp*TOF for simultaneous determination of U-Pb-Th ages and trace element composition of standard zircon grains.

Imaging remains the most speed demanding application in laser ablation. Today, speed, spatial resolution, and sensitivity can be significantly boosted with low dispersion ablation chambers and interfaces. These rapid cells, however, require simultaneous MS if more than 2-3 isotopes have to be imaged. Using the latest fast LA technologies, we introduce a pixel-resolved imaging concept with high-precision laser-MS synchronization. This novel method provides x20 times the speed of standard setups without pixel intermix. We discuss advantages and limitations of this approach for different types of samples.

11:40am - 11:50am

APP-OL 2: 3

Topics: Elemental analysis

Keywords: brines, elemental analysis, ICP-OES

The Analysis of Brines by ICP-OES

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Some of the most challenging samples to analyze via ICP-OES are brines, due to their extremely high dissolved solid content which can cause a variety of instrumental and analytical issues. Brines exist in a variety of compositions, ranging from simple to complex. Simple brines can contain a single component (such as 25-30% sodium chloride), while fracking fluids are examples of complex brines which contain a wide variety of both organic and inorganic components.

Among the challenges which much be overcome when analyzing brines are nebulizer clogging, deposition in the spray chamber, injector, and/or torch, plasma loading, and spectral interferences. All of these issues can affect the analytical results through signal suppression or enhancement, instability, and imprecision. However, these challenges can all be overcome through the appropriate choice of instrumental and analytical conditions. This work will discuss the analysis of various brines by ICP-OES.

11:50am - 12:00pm

APP-OL 2: 4

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: plasma, laser, XUV, beamline, spectroscopy, coincidence

Table-top XUV Plasma-Laser for Chemical Imaging

Davide Bleiner[1,2], Yunieski Arbelo[1], Francesco Barbato[1], Greta Patzke[2]

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Laser action in the extreme ultraviolet and soft X-ray has been demonstrated using laser-produced and discharge-produced hot/dense plasmas as single-pass high-gain media. In the time of large *accelerator-based* X-ray lasers, fundamental and applied research on compact *plasma-driven* X-ray laser carries the promise of bridging the gap between the user and the tools. This demands contributions in (i) better quantitative understanding of the parameter effect on plasma-lasing, and generalization of the empirical models, (ii) assembling compact "table-top" demonstrators with the required robustness to address research and industry challenges, (iii) performing proof-of-principle experiments on “real world” advanced “analytical cases”.

Experiments were run using the newly installed *Beagle*^{Plus} system at the Empa Laboratories. A 0.2ps Nd:glass oscillator feeds a chirped-pulse amplification stage to deliver Terawatt pulses on a target for X-ray plasma lasing. The “*back-end system*”, i.e. compact and close to the application needs, uses also a self-developed pseudospark XUV source for imaging or spectroscopy. A parametric study is also presented.

Nano-analytics were indeed performed on certified reference materials as well as catalysts. Imaging was performed using a self-developed Schwarzschild microscope, with a back-end resolution well-below the resolution of commodity confocal microscopes and without the sample prep for super-resolution techniques. Proof-of-principle spectroscopy experiments using a home-built “frequency-dispersive” Mass Spectrometer as well as X-ray absorption and fluorescence measurements in the so-called HEROS (High-Energy Resolution Off-resonance Spectroscopy) configuration are discussed. The latter tests were validated at the Elettra beamline in Trieste, to be replicated on the *Beagle*^{Plus}.

12:00pm - 12:10pm

APP-OL 2: 6

Topics: Elemental analysis, Environmental sciences

Keywords: Source Apportionment, ICPMS, PM10, Sequential Extraction

Validation of an Online Sequential extraction (OSE) method for the Elemental Characterisation of Fine Dust Sources

Nicole Asante[1], Volker Nischwitz[1], Bernd G. Lottermoser[2]

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Fine dust (PM10) is an ubiquitous component of the atmosphere, comprised of sources both diffuse and numerous. It is well established that fine dust plays an important role in the mechanisms of the atmosphere and critically, is known to have potentially adverse affects on the climate, which in turn affects health of organisms and ecosystems. The need for effective means to characterise and identify significant dust sources is essential for the development of a targeted approach or legislation to assist in the quantification and mitigation of environmental impacts.

Current analytical methods of dust source apportionment often rely on observations of the physical properties of dust, often supplemented by chemical data obtained from total or near-total digestions, and modelling. We have developed an Online Sequential Extraction (OSE) system to attend to the analytical challenges currently not addressed by these methods, for example small sample masses, as well as reduce the number of analytical methods required for the generation of a useful dataset. Using a combination of HPLC pumps and Inductively Coupled Mass-Spectrometry (ICPMS), the OSE system was designed for simplicity and to increase selectivity; elemental fractionation data is collected in real time by implementing a four stage, modified Tessier extraction to elute elemental species from the sample matrices in order of decreasing mobility. These features allow the OSE technique to rapidly elucidate the properties of samples, thereby providing an advantage over the traditional methods of determining total elemental contents or classical extraction schemes.

Model samples representing local sources of dust, including agricultural soil, mine tailings and road dust, were used for method development and validation. By examining the model samples in their “pure” states and in mixtures, we were able to obtain clear demonstrations of the differences in not only the elemental profiles of each sample type, but also the mobility of the elements encountered within them. The data elicited from the OSE procedure were then processed with statistical and chemometric techniques to provide meaningful quantitative data. Using the mixtures of model samples as a simulation for airborne dust as it is encountered in the natural environment; we can apply a source apportionment method such as Positive Matrix Factorisation (PMF) to test the efficiency of our dataset consisting only of elemental fractionation data, as well as the effectiveness of the model in assigning each source. In future we aim to apply this method to real dust samples, and use the OSE as a valuable tool for the reliable identification and management of airborne dust sources.

12:10pm - 12:20pm

APP-OL 2: 7

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metrology in chemistry
Keywords: Matrix-matched calibration, LA-Q-MS, G-Probe

Matrix-matched calibration in LA-ICP-MS of silicate, phosphate and carbonate minerals: application of G-Probe samples

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Laser ablation (LA) sampling in ICP-MS provides fast microelement analysis of a wide range of solid materials without their dissolution, thus decreasing contamination from water and reagents as well as reducing polyatomic isobaric interferences from acid solutions. However, the issue of matrix-matched calibration becomes crucial for LA-ICP-MS due to differences in behaviour during laser interaction and evaporation of solid samples.

There are several approaches to LA calibration: simultaneous supply of standard solutions into a spray chamber [1]; calibration using a set of NIST 61x synthetic glasses and glasses prepared from natural rocks and minerals (basalt, nephelinite, etc.); and pressed synthetic samples (calcium carbonates, phosphates and sulphides produced by USGS).

An extended set of natural glasses for microanalysis calibration is available from the International Association of Geoanalysts (IAG) in co-operation with the USGS. The G-Probe proficiency testing programme has been operating since 2008 and deals with solid samples for microanalysis (LA-ICP-MS, EPMA, EDS-SEM).

Our laboratory took part in G-Probe and has received 13 samples of different composition and provenance: BBM-1G and BSWIR-1G natural basaltic glasses, GSM-1 gabbro; NIST SRM-based basalt and diabase glasses; SL-1G soda-lime glass; GP-MACS synthetic pressed calcium carbonate, GP-MAPS phosphate and some others.

The aim of the present work was to estimate the LA-ICP-MS analysis quality using matrix-matched calibration with G-probe samples of various composition.

All G-Probe samples were analysed using an ELAN 9000 Q-ICP-MS combined with a LSX-500 (Nd:YAG, 266 nm) laser ablation system. ICP-MS operational conditions were optimized using NIST 612. LA parameters (laser energy, frequency, spot diameter) for different types of rocks were chosen on the basis of our previous studies.

For silicate rocks, TB-1 basaltic glass was used for calibration; the remaining samples were analysed as unknowns. MACS-3 and MAPS-4 calibration samples were used for carbonate and phosphate analysis, respectively. A combination of external matrix-matched calibration and internal normalization [2] was used for calculating element concentration.

LA-ICP-MS analysis quality was estimated using Z-scores [3]: if $Z \leq \pm 2$, the results are satisfactory; if $\pm 2 < Z < \pm 3$, the results are questionable and need further elucidation; if $Z \geq \pm 3$, the results are unsatisfactory. Most of the results obtained were in a good agreement with assigned values, and only a small number of them exceeded $Z = \pm 2$.

The study was carried out at the “Geoanalytic” Collective Use Centre. Financial support was provided by RSF grant No. 16-17-10283.

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12:20pm - 12:30pm

APP-OL 2: 8

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-TOF-MS, gemstone

Trace Element Analysis of Gemstones using LA-ICP-TOF-MS

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The main driving force for detailed trace element analysis of gemstones is the demand from the trade for laboratories (such as SSEF) to deliver a scientifically based opinion about the geographic origin of gemstones. This demand is essentially caused by the monetary impact such an origin “label” (e.g. Kashmir sapphire), but also as there is a growing need for traceability of gems due to political (trade bans) or ethical (fair trade).

In this presentation, we will demonstrate the figure of merit of an LA-ICP-TOF-MS system recently installed at SSEF and discuss advantages and disadvantages of this setup applied to routine analyses on gemmological samples. Benefiting from the multielemental capability, one of the most controversial questions in gemmology – origin of gemstones – could be determined with more confidence. The fast data acquisition and simultaneous isotope detection are going to be critical for the quantitative chemical analysis and geological age dating of inclusions, especially, when they are in minimum size.

LA-ICP-TOF-MS has been gaining popularity in the recent years. Recent applications have been focused on high spatial resolution chemical imaging. Applying this developed imaging technique, we would also like to outlook the trend of chemical imaging on gemstones using LA-ICP-TOF-MS.

12:30pm - 12:40pm

APP-OL 2: 9

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Environmental sciences
Keywords: radium, preconcentration, matrix removal, IC-ICP-MS

Determination of radium in natural waters using IC-ICP-MS after on-line preconcentration

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^{226}Ra is a product of the ^{238}U decay series and is the longest-lived isotope of radium, with a half-life of 1602 years. It is one of the most toxic natural radioelements, owing to its high specific activity of 1 pCi/pg, compared with that of ^{238}U at 3 pCi/g. Determination of trace levels of ^{226}Ra is usually carried out by radiometric methods (alpha spectrometry, gamma-ray spectrometry, liquid scintillation counting, etc.). These methods usually require significant sample preparation before analysis, either to preconcentrate ^{226}Ra or to remove the interfering isotopes. In addition, lower detection limits usually require very large sample volumes (> 500 mL) as well as radiometric counting times in the order of days.

Inductively coupled plasma - mass spectrometry is usually not the first choice for this application, as the concentration of Ra in most samples is less than the detection limit of most current ICP-MS systems (< 20 pg/L). Therefore, a preconcentration step is usually required to improve detection limits. While there are many references to batch mode preconcentration in the literature, there are only a handful articles that utilize flow injection for on-line preconcentration and matrix removal. Our research focused on using common cation exchange chromatography columns and systems coupled to a Nexion 350D ICP-MS to evaluate the effectiveness in separating Ra from other matrix components. While most of the columns provided ample separation of Ra and sub-ppq detection limits, a very high capacity column was chosen to avoid column overload after preconcentration. Using this method, common interferences such as $^{88}Sr^{138}Ba^{+}$, $^{87}Sr^{139}La^{+}$, $^{86}Sr^{140}Ce^{+}$, $^{208}Pb^{18}O^{+}$, $^{186}W^{40}Ar^{+}$, $^{209}Bi^{16}O^{1}H^{+}$, and $^{88}Sr^{138}Ba^{+}$ (as well as matrix ions such as Ca and Mg) are chromatographically separated during gradient elution with nitric acid. The method was found to be linear between 0.5 pg/L and 500 pg/L using only a 5-mL sample volume. An internal standard solution (Lu and In) was mixed with the eluant after the column to correct for any possible drift (none was observed). The analytical method was validated by comparing the results of natural water samples using various methods, including alpha spectrometry and a flow injection system similar to the commercially available ESI truFAST system.

This method is a good alternative to common radiometric methods, especially in emergency situations, as it utilizes common instrumentation and provides rapid turnaround time for results with comparable detection limits.

12:40pm - 12:50pm

APP-OL 2: 10

Topics: Metrology in chemistry, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Bose einstein condensate, quantum gas

Few-body physics with ultracold potassium rubidium mixtures

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Within the past decade, research on ultracold atoms has moved from the investigation of their fundamental properties to the application of ultracold samples in quantum simulation and precision metrology. The ability to tailor external potentials freely and to manipulate the interaction strength within the samples has led to numerous advances in the field. In particular, mixed quantum gases have attracted considerable interest, since they offer a wealth of research opportunities. These include the creation of deeply bound dipolar molecules [1], the investigation of few-particle physics [2, 3], the observation of quantum phases in optical lattices [4] and precision measurements [5]. Such mixed quantum gasses can generally be realized by using a single atomic species in multiple quantum states, by using multiple isotopes of the same species, or by using different atomic species. Thus it is possible to realize Bose-Fermi, Bose-Bose or Fermi-Fermi mixtures. Since cooling techniques to achieve ultracold temperatures have become available for an increasing number of atomic species, this leads to a considerable number of possible mixtures. Here, we present the production of dual-species Bose-Einstein condensates of 39K and 87Rb. Preparation of both species in the |F = 1, mF = −1> state enabled us to exploit a total of three Feshbach resonances which allows for simultaneous Feshbach tuning of the 39K intraspecies and the 39K-87Rb interspecies scattering length. Thus dual-species Bose-Einstein condensates were produced by sympathetic cooling of 39K with 87Rb. A dark spontaneous force optical trap was used for 87Rb, to reduce the losses in 39K due to light-assisted collisions in the optical trapping phase, which can be of benefit for other dual-species experiments. The tunability of the scattering length was used to perform precision spectroscopy of the interspecies Feshbach resonance located at 117.56(2) G and to determine the width of the resonance to 1.21(5) G by rethermalization measurements. The transition region from miscible to immiscible dual-species condensates was investigated and the interspecies background scattering length was determined to 28.5 a0 using an empirical model. This paves the way for dual-species experiments with 39K and 87Rb BECs ranging from molecular physics to precision metrology.

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POSTER

POSTER 1 - APP I: POSTER SESSION 1: Applications I

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

POSTER 1 - APP I: 1

Topics: Environmental sciences

Keywords: biological samples, ultratrace analysis, ICP-OES, ICP-MS

Determination of trace elements in healthy and malfunctioning hearts of mice

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Several trace elements are essential for proper functioning of mammalian cells. They are cofactors in various proteins that control fundamental processes such as oxygen transport and storage or energy metabolism. Therefore it is vital that the concentrations of these elements are in a certain range to work properly. Especially chronic deficiencies and overloads of certain trace elements have severe impact on the health of organisms and cause various diseases. Iron deficiency for example is a frequent comorbidity in heart failure.

The aim of the study was to identify potential trace element deficiencies or overloads with major impact in heart diseases such as iron deficiency. For this the contents of biological relevant trace elements in healthy and malfunctioning hearts of mice were determined. Besides, the iron contents in cardiomyocytes of wild-type mice and mice with a genetical depletion of iron regulatory proteins (knock-out mice) were also analyzed.

For the experiments, cardiomyocytes and complete hearts of mice (wild-type and homozygous) have been used. The hearts were dissected, deep-frozen in separated containers, for analysis dissolved by microwave digestion and depending on the concentration levels of the analytes (e.g. Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn) analyzed by ICP-OES or ICP-QMS. All animal procedures were approved by local state authorities.

The analytical challenge was to accurately determine the concentrations of various trace elements in sub-µg/g regions in hearts with fresh masses of several 100 mg and cardiomyocytes with much lower masses. A high-efficient method for ultra-trace analysis, including an elaborate cleaning routine by supra pure acids and water for all components prior to the analysis and clean room conditions, were needed whereas contamination risks by chemicals and equipment were ubiquitous.

It could be shown that for most analytes reproducible analyses in the pg/g to ng/g region were possible, obtaining coefficients of variation for the methods between 1 and 3 % and LODs in the pg/g range for some analytes. Also significant difference of the iron content in cardiomyocytes in wild-type and knock-out mice could be determined. Comparison of the trace element contents in healthy and malfunctioning hearts will be presented and discussed.

POSTER 1 - APP I: 2

Topics: Elemental analysis, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Cobalt, Cobalamins, Inductively Coupled Plasma, Vitamin B12

Feasibility Study for the Determination of Vitamin B12 in Nutritional Products by Inductively Coupled Plasma Mass Spectrometry

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The term vitamin B_{12} is used as the generic descriptor for all cobalamins that exhibit antipernicious anemia activity. The core of cobalamin consists of a corrin ring with a central cobalt atom. The corrin ring has four pyrrole units that are directly bonded to each other, whereas the others are joined by methene bridges. The substituents on the pyrrole rings are methyl, propionamide, and acetamide groups. A cobalt atom is coordinated to the four pyrrole nitrogens. The fifth substituent is a derivative of dimethylbenzimidazole that contains ribose 3-phosphate and aminoisopropanol. One of the nitrogen atoms of dimethylbenzimidazole is linked to cobalt. The amino group of aminoisopropanol is in amide linkage with a side chain of one of the pyrrole ring. The sixth substituent on the cobalt atom can be CN, CH_3, OH, or deoxyadenosyl. The presence of the cyanide ion at the sixth coordination position in cyanocobalamin results from the isolation procedure. Cyanocobalamin is the most stable of the vitamin B_{12}-active cobalamins and is the one mostly used in pharmaceutical preparations and food supplementation. Cyanocobalamin is a neutral, hygroscopic, odorless, and tasteless compound. It is soluble in water (1.2% at 25^{o}C), alcohol and phenol, but insoluble in acetone, chloroform, and ether.

Synthetic forms of Vitamin B_{12} (cyanocobalamin) are widely available and added to many infant formulas and nutritional products. Vitamin B_{12} plays an important role in the functioning of the brain and nervous system, and in the formation of red blood cells. Many analytical methods are available for determination of Vitamin B_{12}, but they require at least six hours of sample preparation time, considerable laboratory set-up, or a proprietary immunoaffinity cartridge for selective extraction. However, the ICP-MS combined with microwave assisted digestion provides a faster way to determine the concentration of vitamin B_{12} in infant formulas and nutritional products. This is possible because of the presence of a Co atom in each molecule of vitamin B12. The concentration of Co can be quickly measured by an ICP-MS to determine the concentration of vitamin B_{12} in food products.

Experimental results to evaluate this procedure demonstrated good accuracy and precision. Accuracy of the method was determined by analyzing pure vitamin B_{12}, a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) [NIST SRM 1640a], and evaluating spike recoveries of vitamin B_{12} in seven SPIFAN products. The difference between the theoretical and experimental Co values for pure vitamin B_{12} (4495.7 pg/g Co) averaged less than 10 % over four days. In the NIST SRM 1640a the average concentration of Co was within the certified range of the SRM. The spike recovery results range from 92-101% with precision values of less than 10 % RSD for vitamin B_{12}. Good linearity (correlation coefficient (r) = 0.9995 or better) was also obtained for Co.

POSTER 1 - APP I: 3

Topics: Sample introduction and sample preparation
Keywords: ICP-MS, sample preparation, geological samples, sintering, fusion, reference materials

Has ICP-MS helped to improve the quality of data obtained from geological samples?

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Unlike many other fields of research, earth scientists can look back to a long tradition of chemical analysis starting in the late 18th century. Analytical geochemists have been involved in 22 years of proficiency testing involving geological materials. During the last decade ICP-MS methods have started to become the dominant measurement principle. The dominance of ICP-MS is based on highly improved measurement selectivity and sensitivity. But has the data quality of reported results improved since the introduction of geological reference materials (RM) and ICP-MS? Results from recent certification and proficiency testing rounds provide insights into the state-of-the-art of whole rock analysis. Generally speaking, ICP-MS has brought vast improvements in lowering detection limits, and made analytes accessible that were previously only quantifiable with separation and enrichment techniques. Rare earth elements are now routinely quantified down to the sub µg/kg range. Thallium, In, Bi, W data are now reported by more and more laboratories. However, the improved sensitivity increasingly leads to reporting measurands in the sub µg/g range without adequate method validation. Other serious problems remain even at comfortable mass fraction ranges. Zirconium and Cr are measurands that previously were quantified by INAA or XRF only are increasingly reported as ICP-MS results. We looked at these two important measurands in more detail in two different rock matrices. The selected rocks were the RM, rhyolite MRH-1, and the Geo*PT*38A material, ultramafic rock HARZ01. A 122 Zr ICP-MS results for MRH-1 provided by 10 expert labs range between 180 and 634 mg/kg while the XRF data vary between 413 and 555 mg/kg. For MRH-1 a certified value of 471 mg/kg was assigned. ICP-MS results for Cr in HARZ01 range from 37 to 3530 mg/kg (*sic*!) while XRF data lie between 1930 and 4504 mg/kg. For Cr the dominant mode (between 2970 and 2990 mg/kg) was assigned as reference value.

Sample inhomogeneity is only a small contributor to the extraordinary variance and thus cannot be the reason for poor performance. Obviously, improvements in instrumentation have not led to a reduction of the measurement uncertainty in these particular cases.

A closer look at the sample preparation techniques and the mineralogy reveals that incomplete acid digestion causes the low recovery of the acid-resistant minerals. Zircon and chromite require HT-HP containment and extended digestion time for complete dissolution when HF/mineral acid is used. Although classical sample preparation techniques such as fusion and sintering remain superior to low temperature acid attack, which is still used in routine analysis.

Thus, the spread of knowledge of matrix-matched sample preparation techniques and the ability or willingness to employ appropriate procedures has not kept up with the rapid improvement of ICP-MS techniques. This inacceptable situation diminishes the success story of ICP-MS in geochemical analysis.

POSTER 1 - APP I: 4

Topics: Sample introduction and sample preparation
Keywords: Detection limits, speed, ICP-OES

ICP Detection Limits Versus Speed of Analysis

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Purpose

Limit of detection is a key characteristic of any ICP method as it defines the „minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero" (EPA, 40 CFR Part 136). It is calculated as three times the standard deviation of a repeated analysis when the concentration reaches zero. Detection limits depend on multiple factors in the process of sample preparation and analysis. An important factor that can enhance or decrease detection limits is the time of acquisition of the signal. With longer acquisition times, short term variations in signal intensities are smoothed out which leads to improved detection limits. However, in this case the improvement of detection limits comes along with an increase in analysis time, often inacceptable for routine applications. The user has to find a compromise between detection limits of the method and speed of analysis. This poster shows a comparison of detection limits achieved with different acquisition times and gives an outlook on ways to improve detection limits without compromising speed. As an example, optimum parameters for a key application of ICP-OES analysis are presented.

Methods

A Thermo Scientific™ iCAP™ 7600 ICP-OES Duo equipped with a Sprint Valve rapid sample introduction system was used in conjunction with a Teledyne CETAC™ ASX-560 autosampler. Detection limits were established with a standard sample introduction, consisting of a concentric nebulizer, cyclonic spray chamber and 2 mm center tube for different acquisition times. For sped up analysis with the Sprint Valve the sample loop size and uptake time were adapted according to the amount of sample being used for the analysis.

Results

By increasing acquisition times from 1 to 60 seconds, an improvement of detection limits of a factor of 5 to 10 was observed, depending on the element wavelength. Further significant improvements are only reached by applying special sample introduction techniques like hydride generation, ultrasonic nebulization and desolvation. A typical analysis time for the key application with optimally adapted sample introduction parameters was less than 70 seconds per sample.

Conclusion

The right uptake timing, tubing length and loop size are key parameters of a rapid analysis with optimal detection limits. For the exemplary ICP-OES application, sufficient detection limits can be reached within minimal acquisition time.

POSTER 1 - APP I: 5

Topics: Environmental sciences

Keywords: chromium-6, water analysis, IC-ICPMS

Optimization and validation of a sensitive IC-ICPMS method for the quantification of Cr (VI) in surface and drinking waters, field study.

Els Van Meenen

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Water-link is a drinking water company, located in the Antwerp region, which provides drinking water for over 2 million people in Belgium and the Netherlands. Surface water, coming from the River Meuse and transported to the catchment areas of our production sites by the Albert Channel, is purified to drinking water with a quality according to the EC regulation 98/83/EU. However, a relatively large number of companies are located alongside this channel and the possibility exists that these companies are pouring their waste water in the channel. Chromium is widely distributed in the environment due to its many industrial applications, e.g. in steel industry and galvanization. ICPMS studies show a varying concentration of total chromium in the raw water (0.30-12.60 µg/L), in
drinking water the concentrations are below the quantification limit (0.07 µg/l). Cr (III) is a nutrient for the human body at trace level, while Cr (VI) is highly toxic due to its high oxidation potential. The need to speciate this last compound at much lower detection limits (ng/l) is therefore necessary. A method was optimized, validated and accredited by the Belgian accreditation organization (Belac) according to ISO 17025 with detection limits of 5 and 7 ng/l for respectively drinking and surface water. Results of a field study will be presented regarding raw- and drinking water produced with different production protocols.

POSTER 1 - APP I: 6

Topics: Elemental analysis

Keywords: inductively coupled plasma, atomic emission spectrometry, carbon, matrix effects

Carbon matrix effects on atomic emission in inductively coupled plasma atomic emission spectrometry

Emma Pérez Hernández, Raquel Serrano Corado, Guillermo Grindlay Lledó, Luis Gras Garcia, Juan Mora Pastor

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Carbon is a concomitant element in biological, environmental and petrochemical samples. Several works in the literature have shown that this element is a source of non-spectral interferences in inductively coupled plasma atomic emission spectrometry (ICP-AES) [1,2]. Thus, it has been observed that carbon presence in the sample significantly affects analyte excitation and ionization pathway under standard plasma conditions. In general, no carbon matrix effects are observed for ionic lines [1]. However, either positive and negative matrix effects have been observed for atomic lines. Positive carbon-based matrix effects are explained by a two-step mechanism where the analyte is ionized by carbon ions and, after an ion-electron recombination process, the population of excited analyte atoms is increased. Elements showing positive matrix effects are As, Hg, I P, Se and Te [2]. Negative matrix effects for atomic lines has been attributed either to the formation of stable stable carbide compounds or deactivation of excited state atoms by collisions with elemental carbon or carbon radicals. Nevertheless, the origin of signal suppression is not really understood so far. In fact, some experimental evidences have shown that carbon matrix effects for this type of lines are somehow related to line excitation energy [2].

The aim of this work is to insight on carbon matrix effects origin for atomic lines in ICP-AES. To this end, the behavior of atomic emission lines of 25 elements covering a wide range of energy values has been studied operating either diluted nitric acid and carbon containing solutions.

References:

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[2] G. Grindlay, L. Gras, J. Mora, M.T.C. de Loos-Vollebregt, Spectrochimica Acta Part B 115 (2016) 8–15.

Acknowledgements: The authors would like to thank the Generalitat Valenciana (Project GV/2014/138) and the Vice-Presidency for Research of the University of Alicante (Project GRE12-19) for the financial support of this work.

POSTER 1 - APP I: 7

Topics: Elemental analysis

Keywords: Petroleum crude oils, ICP-MS

Multi-element analysis of petroleum crude oils using an Agilent 7900 ICP-MS

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In the petrochemical industry, certain analytes are known to impact the performance and value of the final product. Consequently, there are several ASTM methods on the elemental analysis of oils, lubricants and fuels. One example is standard test method ASTM D7111-15a for the determination of trace elements in middle distillate fuels which uses Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). This method is widely used in the industry, but as specifications for fuels become more stringent, some laboratories are favoring the more sensitive analytical technique of ICP-MS, which provides significantly lower detection limits than ICP-OES. To reflect this trend, the first ASTM ICP-MS method for petroleum has been balloted in D0203. This is likely to be followed by an ICP-MS method for petroleum crude oils. This presentation describes how the Agilent 7900 ICP-MS was used to analyze different types of crude oil samples following simple dilution in an organic solution containing *o*-xylene. The aim was to develop a method that is suitable for routine use in the petroleum refining industry, particularly in high sample volume facilities, where turnaround time is critical. For this study, a wide range of samples were tested, and various quality control measures were taken. A series of 18 petroleum crude oil samples were used in the study. The chosen samples had a diverse set of properties; a wide range of American Petroleum Institute (API) gravity, elemental composition, hydrocarbon (H/C) content, and densities were selected. As a performance check, the 7900 ICP-MS was used to analyze diluted NIST 1634c standard multiple times per day with measurements taken over the course of a few months. The results show excellent recoveries for the certified elements V and Ni within + 10%, with good agreement. The recoveries for the non-certified elements As and Se in the SRM were within ± 10%.

POSTER 1 - APP I: 8

Topics: Elemental analysis

Keywords: ICP-MS, Clinical sample, High resolution, Titanium, Collision Reaction Cell

Titanium measurement of clinical samples using CRC-ICP-MS and Sector field-ICP-MS

Tomoko Vincent, Shona McSheehy Ducos

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The titanium physical properties are very high strength, ductile and low density. In the medical science field, titanium or titanium alloys have been employed for the rod and the screw of the orthopedic and the dental implants successfully. However, recently researchers have reported that titanium dioxide (TiO_2) is possible carcinogenic to humans (Group 2B)[(1)].

For this reason, monitoring of the exposure of titanium into the human body is becoming a high potential research. The methodology to monitor exposed samples has to be developed for various categories such as human body fluids, blood, urine and organs.

The concentration of titanium in these samples is very low, usually at or below the $ug \cdot L^{-1}$ level. In addition, accuracy and precision analysis are required, while the sample contains the high matrix. An ICP-MS technique has been used for this type of analysis. However, the major isotopes of titanium are severely interfered by polyatomic species generated by ^{48}Ca, $^{16}O^{32}S$ and others from the sample matrix. Therefore the performance of ICP-MS quantification without collision reaction cell (CRC) for this type of analysis is challenging.

This poster presentation demonstrated the trace titanium analysis of human reference materials using most recent CRC-ICP-MS and sector-field ICP-MS.

Reference

(1) Website of *International Agency for Research* on Cancer http://monographs.iarc.fr/ENG/Publications/techrep42/TR42-4.pdf

POSTER 1 - EL: POSTER SESSION 1: Elemental analysis

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

POSTER 1 - EL: 1

Topics: Elemental analysis, Environmental sciences

Keywords: technology-critical elements, ICP-SFMS, enrichment techniques

Technology-critical and hazardous elements in the environment.

Lisa Fischer[1], Geoffrey Smith[2], Kenneth W. Bruland[2], Stephan Hann[1]

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This work is focused on developing emerging analytical tools to cope with the increasing role that technology-critical and hazardous elements play in our environment. Given the well-known potential dangers posed by toxic elements such as heavy metals for both natural environments and human health, analytical methods capable of accurately monitoring their distribution in environmental samples are essential. To address this goal, advanced and robust methodologies capable of selectively and quantitatively analysing these elements will be developed to accurately map the distribution of these elements in our environment. The analytical methods investigated will involve ICP-(SF)-MS in combination with off-line and on-line matrix-separation and enrichment techniques such as solid-phase extraction and cold vapour technique. This combination will provide an improved and valuable set of analytical methods capable of mapping of elements in the environment at trace- and ultra-trace levels, which is invaluable for our understanding with respect to the environmental fate and eco-toxicological potential.

POSTER 1 - EL: 2

Topics: Elemental analysis

Keywords: implants, antibacterial coating, animal study, degradation, silver

Ultra-trace analysis of silver in biological samples

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Initiated by the increasing antibiotic resistance the use of antimicrobial silver is focused for different implant materials. This study is concerned with permanent TiAl6V4 implants, in which silver nanoparticles are incorporated into surface layers. The behavior and the accumulation within different organs and tissue of alloying elements of implant materials are of specific interest to assess their possible influence on the body. To evaluate the accumulation of the implant components in rat organs TiAl6V4 discs were implanted subcutaneous for different residence times (3 and 7 days, 4 weeks and 6 months). For a comparison and to get information about background values in the different rat organs control studies with HDPE implants were performed under the same conditions.

Most of the element values are expected to be extremely low, so all containers, auxiliary devices and other utilities have been purified extensively. To avoid contamination a specific cleaning procedure were implemented. To convert the organs to solutions microwave digestions were performed using ultrapure water and sub boiled nitric acid. Dual or three-fold determinations were performed as long as sufficient sample-mass was available.

The accumulation of silver was analyzed in selected organs like liver, kidney, spleen, brain and tissue near the implanted discs. The silver amounts in the organs were analyzed via ICP-MS using an external calibration. The standard solutions were prepared with 1% sub boiled nitric acid to adjust the matrix. To compensate temporal fluctuations a dynamic drift correction was performed after every seventh measurement to adjust plasma effects which are caused by the biological matrix. The silver amount and the alloying elements in the tissue near the implanted discs were analyzed via ICP-MS and ICP-OES for a comparison. The low amounts of alloying elements within the organs did not allow an ICP-OES determination.

Regarding the silver accumulation an initial increase in the silver amount within all analyzed organs (liver, spleen, kidney) after the first days was observed. The silver amount decreased with increasing implantation time, so that after 6 months background level was almost restored. After 4 weeks and 6 months implantation time increased amounts of titanium, aluminum and vanadium were determined in the tissue near the implanted discs. The silver amount was also increased at every implantation time, although the high standard deviation between the similar time groups impedes a valuation of a trend formation. From the present results it is difficult to decide between a long-term accumulation of silver within the tissue or a continuous release of silver ions which is the intended antibacterial effect of implementing these nanoparticles in the surface of TiAl6V4 implants.

POSTER 1 - EL: 3

Topics: Elemental analysis

Keywords: MP-AES, food

Minerals determination in food matrices using MP-AES

Marine Nicolas, Céline Fragnière Rime, Sylvie Merinat, Brigitte Rey, Eric Poitevin, Nicola Galaffu

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Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) represents a completely new multi-elemental analysis technique that has been designed to improve analytical performance and productivity, while decreasing operating costs by eliminating the flammable and/or expensive gas requirements used in typical elemental analysis techniques (e.g. FAAS, ICP-AES). Thus, new methods adapted to this new type of microwave excited nitrogen plasma and its respective temperature, to the specific introduction system and optical parameters need to be developed.

A method has been developed and validated for food matrices (e.g. flour, health care products and cereals based products) for the simultaneous quantification of Calcium (Ca), Iron (Fe), Potassium (K), Magnesium (Mg), Sodium (Na), Phosphorus (P) and Zinc (Zn) by Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) after an acidic microwave assisted digestion.

The method performances such as linearity, sensitivity, selectivity, precision, trueness and measurement uncertainty established according to ISO/IEC 17025 norms were investigated. The results obtained with the MP-AES were comparable to those obtained by ICP-AES using Official Method AOAC 2011.14 as standard.

Although the validation was performed only on few matrices, the method is expected to work with samples covering the whole AOAC food triangle. Next step will be an extension to additional elements such as Copper (Cu), Aluminium (Al) or Manganese (Mn).

POSTER 1 - EL: 4

Topics: Sample introduction and sample preparation, Elemental analysis, Environmental sciences
Keywords: trafic pollution, needles, ICPQQQ, element determination

Element concentrations in needles as an indicator for traffic influence on the environment

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To investigate a potential influence of traffic pollution (influence of road salting included) on the environment, samples of 1-year-old and 2-year-old needles of Norway spruce - *Picea abies* (32 samples) and Scots pine - *Pinus sylvestris* (70 samples) were collected from two sites differing in traffic loading. Spruce trees were selected because of their abundance and high sensitivity to salinity [1,2]. They are known to be good indicators for urban pollution [2]. The 1- and 2-year old needles were analysed separately. Additionally soil samples were taken from each sampling site.

The needles were crushed, milled and then digested in quartz vessels with HNO_3 at a temperature of 250°C for 30 min and a loading pressure of 40 bar Argon using an ultraCLAVEIII (EMLS GmbH, Germany). The soil samples were sieved, milled and digested in Teflon® vessels in microwave system (SW-4+, Berghof, Germany) at a temperature 200°C and pressure 30 bar. Concentrations of a wide range of elements were determined including heavy metals and PGEs from road operation, alkali metals and Cl from winter road maintenance and biogenic elements such as P and S. Analyses were performed on a triple quadrupole ICPMS (ICPQQQMS, Agilent Technologies, Japan). Data were evaluated for the two sites differing in traffic loading. Statistical evaluation was used for interpretation of complex interaction patterns between element concentrations in different age needles based on localities character including distance from the road and element concentration in soils.

References

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POSTER 1 - EL: 5

Topics: Elemental analysis

Keywords: Aluminum, soy-based food, total content, soluble fraction

DETERMINATION OF ALUMINIUM IN SOY-BASED FOOD: TOTAL CONTENT AND SOLUBLE FRACTION

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Among soy-based food are soft drinks that use ingredients like soy extract, isolated or concentrated textured protein or soy and/or other soy protein sources that present 70% of caseína[1]. Its consumption has increased in recent years due to its association with the prevention of cardiovascular diseases, cancer, osteoporosis and symptoms related to menopause. Besides minerals and vitamins, its composition presents trace elements whose essential character is not yet known. Among them the aluminum stands out, which has aroused the attention of the scientific community and regulator organizations because of their possible association with degenerative diseases such as Alzheimer's disease. The Joint FAO/WHO Expert Committee on Food Additives established a provisional tolerable weekly intake (PTWI) for Al in 2 mg/kg of body weight. This Committee still concluded that the PTWI may be exceeded by individuals, especially children, who consume large amounts of food with additives in their composition and soy-based products[2]. However, it is known that after eating, the food components undergo biotransformation processes along the gastrointestinal tract[3]. Then, the evaluation of bioaccessible fraction of trace elements is important for the correct assessment of the risk associated with the ingestion of food.

The objective of this work is the evaluation of the total content and the soluble fraction of aluminum in eight samples of soy-based foods with orange, apple and grape flavors.The evaluation of the bioaccessible fraction consisted of the simulation of the gastric and intestinal juice, using the pepsin solution in an acidic medium (1.0 mol L^{-1} HCl) and a solution containing pancreatin and bile salts in alkaline medium (0.1 mol L^{-1} NH_4HCO_3), respectively. For the determination it was used the solution obtained from microwave acid digestion (time = 30 min; = 140° C maximum temperature). The aluminum quantification was carried out using an ICP OES instrument (5100 VDV, Agilent Technologies,Japan). The ICP OES parameters used were radio frequency power of 1350 W; plasma argon flow rate of 12 L min^{-1}; auxiliary argon flow rate of 0.5 L min^{-1} and a nebulization gas flow rate of 0.55 L min^{-1}.

It was found that the total aluminum content in soy food samples ranged between 145 and 1375 µg L^{-1}, being observed the following behavior: $[Al]_{soya\ beans} < [Al]_{isolated\ soy\ protein} < [Al]_{soy\ extract}$. Considering the bioaccessible fraction, only samples with soy extract in its composition showed quantifiable aluminum content (> 11 µg L^{-1}) that correspond to 38 and 70% of the total content.

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POSTER 1 - EL: 6

Topics: Elemental analysis

Keywords: ICP QQQ MS, MS-MS performances, heavy metals, hair

Application of ICP-QQQ -MS for multielemental trace determination of As, Cd, Cr, Hg, Mn, Ni, Sb, Se, Sn and Pb in human hair

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With the wide range of metallic contaminants discharged in the environment, studying the human health requires a growing number of elements to be monitored in biological samples since compelling evidences of their specific roles in the pathogenesis and progress of many diseases have been reported. Biomonitoring the exposure to heavy metal is commonly conducted by blood and urine. Hair analysis has been suggested as a suitable biomarker of environmental pollution and occupational exposure since it can depict history of extended period of exposure[1]. In complex biological matrices, tenaceous interferences can hinder the accurate determination of metals at trace levels. This study describes a method for the simultaneous determination of 10 trace elements in hair samples using ICP-QQQ technology after microwave acid digestion. Combining the power of the MS/MS high energy Helium mode (HEHe) with the MS/MS O2-mass shift mode, the method offers great analytical performances with detection limits reaching 0.01 µg/g for As and Ni; 0.02 µg/g for Cd, Cr, Mn, Sn, 0.005µg/g for Sb ; 0.03 µg/g for Pb ; 0.04 µg/g for Se and 0.05 µg/g for Hg. These limits are 3 to 25 lower than those obtained in a recent study realized on an HR ICP MS [2]. Recoveries of known amounts of metals added to the samples varied from 94.6 to 106.9%. The proposed method was applied for the determination of metal contents in hair samples of twenty healthy subjects. Results showed variation between sujects. The metal concentrations were in the same range with the reported data. Cd levels in hair were very low approaching the method detection limit. Results of hair Sn of some subjects were relatively higher than those reported for healthy unexposed subjects. The reported results for Sb an Sn could be very useful since little has been reported about their levels in human hair. Despite the small sample size, the reported results of trace metals in hair samples of healthy Tunisian subjects may be useful for environmental exposure assessment or comparisons studies when establishing reference values of heavy metals in exposed population.

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[2] E. V. Buononato, D. De Luca, I. C. Galeandro, M. L. Congedo, D. Cavone, G. Intranuovo, C. M. Guastadisegno, V. Corrado. Assessment of environmental and occupational exposure to heavy metals in Taranto and other provinces of Southern Italy by means of scalp hair analysis **(2016)** 188:337

POSTER 1 - EL: 7

Topics: Elemental analysis

Keywords: ICP-MS, silver, release of silver, wound dressings, validation

DETERMINATION OF SILVER IN WOUND DRESSING MATERIALS BY ICP-MS

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Silver is widely used as an antimicrobial agent in various medical products such as ointments, solutions and especially wound dressings. The medical products contains the small amount of silver in different forms (nanoparticles, proteins or salts) and therefore rapid consumption of small amount of silver species as well as the presence of the nitrates can slow down the healing process. On the other hand, the high concentration of silver can result in the dyeing of tissues and other medical complications. Currently, there is a strong demand for the development and validation of method for the sensitive screening of the silver content in medical devices.[1,2]

In this sense, presented work has been focused on evaluation of the total silver content and silver released from four Ag-based dressings, namely Aquacel Ag (ConvaTec, Czech Republic), Mepilex Ag (Mölnlycke Health Care, Czech Republic), Atrauman Ag and Cosmopor Antibacterial (HARTMANN- RICO, Czech Republic). Samples were digested by microwave system with mixture of HNO_3 and H_2O_2. The amount of Ag was quantified by ICP-MS (Agilent 7700x; Agilent Technologies, Japan) and the structure of the materials was characterized using scanning electron microscopy-energy dispersive X-ray spectrometry. ICP-MS method was verified by the following parameters: limit of detection (LOD), linearity, repeatability, trueness and intermediate precision. LOD was determined as 3.5 $\mu g.g^{-1}$.Trueness was evaluated by recovery tests. Repeatability results ranged between 18 and 20 %. Furthermore, the inhomogeneity in the distribution of silver was observed by SEM-EDS.

Finally, ICP-MS method was successfully applied for the screening of silver in different dressings. Aquacel Ag gives the best result after decomposition in 0.2 $mol.l^{-1}$ NaOH with stirring on a vortexer at room temperature. Moreover, the total silver content in this type of dressing did not match the declared amount of manufacturer. The amount of released silver in deionized water and physiological solution strongly depends on the silver form and the type of solution. In addition, the balance of silver in solutions after decomposition was studied as well.

Acknowledgements

This research was supported by the project LO 1305 of the Ministry of Education, Youth and Sport of the Czech Republic.

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POSTER 1 - EL: 8

Topics: Elemental analysis, Environmental sciences

Keywords: Offshore, Trace Elements, ICP-MS/MS, Anodes, Sea water

Multi-elemental characterization of anode materials used for cathodic corrosion protection of offshore structures using ICP-MS/MS

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In the course of the renewable energy boom in the beginning of the 21st century, the wind energy industry moved to offshore areas due to the increasing lack of suitable inland sides.

Up to June 2016, 733 wind power plants (WPP) with a total power of 3,213.42 MW have been installed in the German North Sea area. Additional 102 WPP with a power of 338.8 MW have been installed in the German Baltic Sea. Beside this additional 54 WPP (324.0 MW) without grid feed as well as 142 foundations were erected in the North Sea, which were not yet equipped with WPP. By the end of 2017, the maximum connection capacity to be allocated by law is 7.7 GW for projects that can be implemented by 2020. This corresponds to a number of up to 700 additional wind power plants. In total the approved wind energy parks currently cover already 15 % of the German exclusive economic zone

The offshore wind foundations that are exposed to seawater or buried in marine sediments often employ cathodic protection using galvanic anodes to guard against corrosion. Up to 10 t anode material for each WPP is required. Since the cathodic protection by galvanic anodes results in the continuous dissolution of the used alloy (e.g. mainly Al and Zn based) the anodes have to be replaced on a regular basis. Beside Al and Zn, which are the most frequently used elements for sacrificial anodes, the used alloys often contain various other metals as impurities, which are also released into the surrounding water body upon dissolution of the anode material. Unfortunately, up to now no information is available about potential long-term effects on the surrounding marine environment related to the release of different contaminants from such large-scale infrastructure.

Therefore this contribution will present some first results obtained during the development of a suitable analytical method allowing the multi-element characterization of aluminum and zinc-based sacrificial anodes of different manufactures used for the protection of offshore structures. Different acid mixtures have been tested to allow the total dissolution of the different tested materials prior to multi-element analysis via ICP-MS/MS (Agilent 8800, Agilent Technologies, Waldbronn, Germany).

POSTER 1 - EL: 9

Topics: Elemental analysis

Keywords: ICP-QQQ, high-purity chemicals, hydrogen peroxide

Analysis of ultra-pure water and high-purity chemicals with the Agilent 8900 ICP-QQQ

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Continuously evolving requirements for higher-performance electronics and smaller architecture devices have led to demands to analyze a wider range of impurities at lower concentrations in the chemicals used during semiconductor manufacturing. Impurity elements are now measured at sub-ppt (ng/L) to ppq (pg/L) level in many high-purity process chemicals, and there is an increasing need to analyze non-metals such as sulfur, phosphorus and silicon in ultra-pure water (UPW) and some chemicals.

Quadrupole ICP-MS (ICP-QMS) with collision/reaction cell (CRC) is the most widely used technique for analyzing trace impurities in UPW and semiconductor process chemicals. Its advantages include low detection limits for most elements, fast multi-element analysis, and ease of use. However, in the case of conventional quadrupole ICP-MS, non-target ions enter the cell and may pass through to appear in the spectrum as overlaps on target analyte product ions, or may react with the cell gas to form new interfering product ions. In either case, there is a risk of non-target ions of product ions appearing in the spectrum and causing errors.

The recently introduced technique of triple quadrupole ICP-MS (ICP-QQQ) offers a more reliable and consistent approach to resolving spectral interferences compared to conventional quadrupole ICP-MS. ICP-QQQ has an additional quadrupole mass filter (Q1) in front of the cell, to control the ions that can enter the cell. This ensures that the reaction processes in the cell are consistent, minimizing the risk of non-target product ion(s) being formed from the matrix elements or other analyte ions.

The 8900 ICP-QQQ is Agilent's second generation ICP-QQQ featuring MS/MS capability, with higher sensitivity, axial acceleration cell and lower sulfur and silicon backgrounds compared to the previous 8800 model. The 8900 ICP-QQQ is easy to setup and use for typical applications, but also offers a very flexible approach to achieving optimum method settings for the most effective interference removal, as needed for the lowest detection limits required in the semiconductor industry. Software tools such as autotuning and Method Wizard help with selection of the best cell gas, flow rate and cell voltages, while predefined methods assist with identification of the best measurement mode and product ion for a given analyte cell gas combination.

For routine analysis in a production or quality control environment, it is beneficial to use a method with the minimum number of different tune modes. In this study, we investigated the performance of the 8900 ICP-QQQ for low-level determination of impurities in pure water and high-purity chemicals. We will describe method optimization for routine analysis using standard cell gases (helium, hydrogen, oxygen and ammonia), and present the results obtained for ultra-low level analytes in high purity reagents, ultra-pure water and hydrogen peroxide.

POSTER 1 - EL: 10

Topics: Sample introduction and sample preparation, Elemental analysis
Keywords: Radium, seawater, trace metals

Online separation and determination of 226Ra and trace metals from high salinity wastewater and seawater

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Traditional methods for low level ^{226}Ra determinations require elaborate sample preparation, long sample holding times and/or long detection times. In response to these constraints, an online solid-phase extraction method combined with ICP-MS to separate and purified low level ^{226}Ra from matrix in high salinity liquid samples such as high salinity wastewater or seawater was developed in this study. Using this analytical protocol, other trace elements from the sample can be determined during the separation of Ra from the sample matrix. The AG 50w x 8 cation exchange resin, Sr Spec resin and Nobias Chelate resin were used in a follow controlled automated system which was programmed to control the separation and pre-concentration of Ra and inline dilution of other elements. Method optimization achieved high Ra recovery (95$\pm$5%) and a method detection limit of 27fg L^{-1}(10 mBq L^{-1}) of ^{226}Ra using 25ml of sample. In addition, this method also achieved up to 1000 times online dilution for other metals. There is significant potential to apply this system to online determination of other radionuclides.

POSTER 1 - EL: 11

Topics: Elemental analysis

Keywords: ICP-MS, Biopharmaceuticals, IgG, Vitamin B12

Biopharmaceuticals: ICP-MS for the determination of the origin of the colour of protein preparations

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Purpose

In pharmaceutical industry the quantification of trace elements is a very helpful method to support the optimization of production processes and for troubleshooting.

For purification an immunoglobulin was loaded on a Protein A column in four cycles due to the high volume. From cycle to cycle an increasing pink staining was observed. The Protein A eluates of the four cycles were analyzed by ICP-MS to identify any differences in the trace element composition that allow any conclusion on the origin of the increasing pink colour.

Methods

The Protein A eluates as well as the related loads of the four cycles were diluted 1:10 with 2 % nitric acid, mixed and span for 5 minutes at 16 000 x g. Supernatants were decanted into sample vials and analyzed by ICP-MS (Agilent, 7500cx) using the nogas- as well as the ORS- mode.

Results

Out of 27 elements analyzed, Co could be identified as being increased in the Protein A eluates from cycle to cycle corresponding to the increasing pink staining, the related loads showed equal Co levels. Co is a co-factor of Vitamin B12 which is known for its red/pink colour and is component of the culture media used in the fermentation process.

Conclusion

ICP-MS is a good and convenient method to support the production of biopharmaceuticals by analyzing the harvest or eluates of different purification steps, to optimize processes and for troubleshooting. It can also help to understand biochemical processes during the fermentation of the cells.

POSTER 1 - EL: 12

Topics: Elemental analysis, Environmental sciences

Keywords: Atomic Spectroscopy, Elemental Analysis, Geological

Elemental Analysis of Challenging Geological Samples Made Easy

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Analytical chemistry is an important tool in the mining process. Whether it is to determine a single element like gold, silver or platinum group metals in ore grade material or even to map geochemical composition of rocks, such results are essential to ensure the commercial viability and the environmental impact of any mining process. However, the analysis of geological samples is considered very challenging because these samples are complex, heterogeneous mixtures of minerals. They are formed from a multitude of small grains each with a different composition.

Today's analytical technics such as ICP-MS, ICP-OES and AA provide a viable solution for inorganic analysis. With simplicity, flexibility and reliability, many analytical systems are design with geological and mining industry in mind. They offer high productivity and accurate results in the most challenging sample matrices including.

This poster will show that inorganic analytical instruments made analysis of mining samples easy in terms of sample preparation, method development, accuracy, removal of interferences and stability. Results in real samples and Standard Reference Materials would be shown and discuss.

POSTER 1 - EL: 13

Topics: Elemental analysis, Environmental sciences
Keywords: REE, ICP-MS, trace analysis

REE matrices – how accurately determine contaminations?

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Rare earths have unique magnetic, luminescent, and electrochemical properties that used in many technologies such as aerospace, health care, clean energy, electronics and transportation. However, often function of high tech devices that incorporate REE depends on the cleanliness of used materials.

The objective of this poster is to investigate the capability of the current ICP-MS instrumentation for accurately determining contaminations in high purity REE. It would be shown that the ICP-MS with the universal cell technology can efficiently remove many spectral interferences created by REE matrices, Ar, O2, H2 and acids.

POSTER 1 - EL: 14

Topics: Environmental sciences
Keywords: ICP-QQQ, MS/MS; interference; high-purity barium carbonate; Eu; Sm

Accurate determination of Eu, and Sm in ultra-pure barium carbonate materials by ICP-QQQ

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ABSTRACT: $BaCO_3$ is a precursor material that undergoes solid-state reaction with TiO_2 to form $BaTiO_3$, which is one of the most widely used ferroelectric materials for multi-layered ceramic capacitors with high capacitance density. Conventional technique of $BaCO_3$ preparation is based on high-temperature reduction of barite (natural barium sulfate). The presence of metal ions and rare earth elements (REEs) in barium raw materials (witherite and barite) would affect the quality of the final product. Numerous studies have been reported concerning impurity analysis in the barium matrix using different methods. Inductively coupled plasma–mass spectrometry (ICP-MS) is a robust analytical tool that can achieve detection limits at ppt or sub-ppt level for most elements. However, when analyzing barium samples using conventional quadrupole ICP-MS (ICP-QMS), the measurement of some trace REEs (e.g., Nd, Gd, Sm, and Eu) is compromised by overlaps from intense polyatomic interferences, such as BaO^+ and $BaOH^+$. Several sample-pretreatment techniques, such as flow injection on-line solid phase extraction, and ion exchange chromatography, have been developed to separate the trace REEs from the Ba matrix prior to ICP-MS detection. Although satisfactory results could be achieved by these sample preparation techniques, these approaches require cumbersome pre-separation procedures.

Compared with conventional quadrupole ICP-MS, triple quadrupole ICP-MS (ICP-QQQ) with MS/MS operation offers the capability to accurately measure Eu^+ and Sm^+ at low concentrationsin ultra-pure $BaCO_3$ materials using both NH_3 on-mass mode and O_2 mass shift mode. The level of interferences with ICP-QQQ were two or three orders of magnitude lower than with ICP-QMS. Using ICP-QQQ with MS/MS mode, the DLs (limits of detection) of Eu^+ was 4.0 ng kg^{-1} to 15 ng kg^{-1}, and DLs of Sm^+ was 20-40 ng kg^{-1}, with spike recoveries ranging from 100%–110%. For the analysis of high-purity barium samples, ICP-QQQ with MS/MS mode can easily meet the requirements of ppt or sub-ppt level impurity analysis.

POSTER 1 - EL: 15

Topics: Elemental analysis

Keywords: osmium, ICP-MS, pharmaceutical products

CHALLENGES IN OSMIUM DETERMINATION IN PHARMACEUTICAL PRODUCTS BY ICP-MS

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The determination of elemental impurities, undesirable components without therapeutic benefit, in pharmaceutical products has recently gained interest in quality control laboratories of pharmaceutical production. The elemental impurities, particularly heavy metals may be introduced into the drugs from different sources. Consequently, their levels should be strictly controlled in drug products due to their adverse effect on human health.

Without any doubts osmium belongs to elements which determination in pharmaceutical products after microwave digestion with the use of oxidative acids is challenging. This contribution will present the comparison of approaches described in the literature and procedures developed in our laboratory that are based on complexation of osmium, reduction of OsO_4 and cooling.

Acknowledgements

The authors gratefully acknowledge the support from the Ministry of Education, Youth and Sports of the Czech Republic LO 1305.

POSTER 1 - EL: 16

Topics: Elemental analysis

Keywords: ICP-QQQ, high purity metal, high purity copper, semiconductor, reaction cell

Determination of ultra-trace level impurities in high-purity metal samples by ICP-QQQ

Naoki Sugiyama, Michiko Yamanaka

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Metals such as Cu, Al, Ta, W and Hf are used in interconnects, diffusion barriers and metalized thin films in semiconductor devices. Very high purity metals are required to ensure high performance, reliability and high production-yield of the devices. ICP-MS is a sensitive, multi-element technique used for the quality-control of these metal materials; but the application is not easy due to the requirement for ultra-low level impurity measurement in the relatively high-matrix metal sample digests.

A particular challenge is the ultra-trace measurement of alkali elements in the presence of the high matrix. Cool plasma is accepted in the semiconductor industry as a reliable technique to remove argon-based interferences such as Ar^+ and ArO^+ to enable low-level analysis of ^{40}Ca and ^{56}Fe. Cool plasma can also be applied to the analysis of the alkali and alkaline earth elements, providing lower background equivalent concentrations (BECs) than normal hot plasma conditions. This is because the low temperature plasma prevents the reionization of traces of the easily-ionized elements (EIEs) on the interface cones and ion lens. However, the cooler plasma also has poorer matrix tolerance, so is not suitable for the analysis of high matrix metals samples.

In this paper, we describe a new approach to the measurement of ultra-trace impurities in 0.1% high purity copper, using ICP-QQQ. The method uses a new design of ion lens that addresses the requirements of high matrix tolerance and ultra-low level measurement of the alkali and alkaline earth elements. The new lens, which is optional on the Agilent 8900 ICP-QQQ, has a unique geometry which minimizes background signals from EIEs on the skimmer cone. The new lens provides sufficiently high sensitivity to allow determination of ultra-trace impurities, combined with low EIE background signals under the hot plasma conditions required for high matrix analysis.

To provide a rapid method for production control and to minimize sample matrix loading, we investigated whether a single reaction cell mode could allow all elements to be measured free from interferences. A mixture of H_2 cell gas at 7 ml/min and O_2 at 0.23 ml/min was found to work well to remove all spectra interferences while maintaining good sensitivity for all measured elements. Using MS/MS mode on the 8900 ICP-QQQ eliminated the risk of interferences due to interelement overlaps or new, cell-formed product ions.

Details of the new method will be described, and figures of merit for the analysis of 50 elements in 0.1% high purity copper sample will be presented. The elements measured included the alkaline elements Li, Na and K, which can suffer elevated backgrounds due to reionization. Results will also be presented for elements that are difficult for conventional quadrupole ICP-MS (Si, S and P), and elements which suffer from Cu-based polyatomic interferences, such as Ru, Rh and Pd.

POSTER 1 - EL: 17

Topics: Elemental analysis

Keywords: multi-element, screening, matrix effect, response curve

Panoramic analysis of water based process streams for recovery of technology-critical elements; comparing ICP-OES, ICP-MS and ICP-HR-MS

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Waste or secondary resource? A growing concern. Not only towards an ecofriendly and sustainable society, but recycling has also economic and geopolitical importance, especially if technology-critical elements, such as rare earth elements, are involved. A new technology to recover low concentration metals from water based industrial process streams is currently being developed by VITO (Flemish Institute for Technological Research), Ghent University and University of Leuven. Knowing which and how many metals are present in potential secondary resources is a prerequisite. Therefore, panoramic analysis is needed, i.e. one screening allowing to determine as much elements as possible.

However, water based process streams often have high salt concentrations and might be loaded with organics. Hence, matrix effects are to be expected and an evaluation of the performance of panoramic analysis procedures for this type of samples is needed. Therefore, five different analytical methods were compared; three commercially available and two modified methods. The first method runs on ICP-OES, uses a one point calibration for all elements and Ar emission to correct for response fluctuations. The second one runs on ICP-HR-MS, also uses one point calibration for all elements but Rh as an internal standard. Method three uses an ICP-MS device where an all element response curve can be updated without the need to calibrate all elements individually and uses Rh as internal standard. Method four is similar to method three, but µ-flow injection is used instead of continuous injection. Method five uses automated standard addition of all elements on an ICP-MS.

Comparison of these five methods is based on accuracy, precision, detection limits, linear dynamic range and drift. Therefore, standards, blanks, artificial matrices and real samples are analyzed. Also recovery of spikes and over time reproducibility are evaluated.

The results will indicate which of the five methods is preferred to screen water based process streams for elemental composition and might suggest which way to go for further improvements.

POSTER 1 - FUN: POSTER SESSION 1: Plasma source fundamentals

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

POSTER 1 - FUN: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Thomson scattering

Effect of plasma turbulence on the Thomson scattering process

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The influence of plasma turbulence on the Thomson scattering process is investigated in turbulent plasmas by the scattering of electromagnetic waves. The Thomson scattering cross section in turbulent plasmas is obtained by the fluctuation-dissipation theorem and plasma dielectric function as a function of the diffusion coefficient, wave number, and Debye length. It is demonstrated that the turbulence effect suppresses the Thomson scattering cross section. It is also shown that the turbulence effect on the Thomson scattering process decreases with increasing thermal energy. The dependence of the wave number on the total Thomson scattering cross section including the turbulent structure factor is also discussed.

POSTER 1 - FUN: 2

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: ICP-MS, matrix suppression, plasma space charge, skimmer cone positive voltage, compensate the plasma DC potential

ICP-MS matrix suppression cancelation effect after applying the positive voltage to the skimmer cone

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PlasmaQuant MS is a high sensitivity ICP-MS with ReflexION, 3D focusing, 90 degree Ion Mirror optics and efficient plasma generation coupled to a two cone Compargue interface. In some cases matrix suppression can reduce the sensitivity of the high TDS samples. Matrix suppression can be explained by the additional plasma space charge formation happening within the 'zone of silence' due to the electron escape mechanism. Our data/model suggests that the initial DC plasma potential space charge of +1…+3V is formed near the skimmer cone tip under the dry Hot Plasma. Introducing high matrix samples can typically add +1…+2V to the initial plasma potential depending on the plasma T and the 1st ionization potential of the sample matrix.

In our opinion the additional DC plasma potential is the reason for the matrix suppression when the grounded skimmer cone is used. It is obvious that the grounded skimmer cone transmission characteristics are not in optimum when dealing with plasma and DC potential within the 'zone of silence'. The skimmer cone positive voltage (equal/higher to the DC plasma potential) has to be applied to the skimmer to reduce/eliminate matrix suppression effect.

Instrument: PQMS Elite (Analytik Jena) with modified Compargue interface (positive skimmer cone bias, BOOST) was used during the experiment.

Experiment idea: Applying the positive voltage to the skimmer cone to compensate the plasma DC potential with a goal of reducing/canceling the matrix suppression.

Samples: 15 analyte elements and 6 matrix elements with different mass and 1st ionization potential of the atoms were used. The samples matrix concentration (0.001-0.1 g/dm^3) and skimmer bias (0, +2, +4, +6, +8V) were utilized during the experiment.

The result: The positive skimmer cone bias can significantly reduce and in some cases virtually eliminate the matrix suppression for all of the matrix elements, even when their concentration in the samples is 0.1 g/dm^3.

Discussion: The space charge formation mechanism and interface operation details are discussed.

POSTER 1 - FUN: 3

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: enclosed ICP, enclosed ICP-OES

Reduction of the Argon Consumption to less than 2 L min-1 by Gas Recycling: A new Approach in Inductively Coupled Plasma Optical Emission Spectrometry

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Inductively coupled plasmas (ICPs) are used for spectrochemical analysis for more than five decades. Though great progress was made in the instrumentation used, the general mode of operation – a plasma that is formed under atmospheric pressure and expands from the torch into the surrounding air – has not changed. There were several attempts to operate the ICP as a “sealed source”, but various problems associated with the stability of the material enclosing the source and the introduction of sample were encountered.

In this contribution, we introduce an innovative interface between the torch and the entrance optics for inductively coupled plasma optical emission spectrometry (ICP-OES). The plasma is formed inside a standard torch but expands into a metallic enclosure rather than into the open air. This enclosure is mounted directly on the optical plasma interface of a commercial axially viewed ICP-OES (Ciros Vision EOP, Spectro, Germany).

By operating the ICP as an enclosed source, it is possible to collect all the argon initially supplied to the torch, cooling and cleaning it and feeding most of the argon back to the outer gas port of the torch. Thereby, the total argon consumption could be reduced from 14 to 1.4 L min^{-1} using a standard torch. Most importantly, the enclosed ICP could be operated even at the maximum power level the used RF generator was able to deliver (1700 W) and standard spray chambers and nebulizers could be used.

The excitation- and rotational temperature of the plasma were identical when comparing the traditional setup with the enclosed plasma interface. However, the limits of detection (LOD) and limits of quantification (LOQ) of 27 elements investigated were degraded about 5-fold, though this fact can be expected to stem from a change of the observed zone in the plasma caused by the slight overpressure of 2000 Pa within the interface. Though the enclosed plasma interface was located close to the load coil, the RF power coupled to the interface was well below 1 W and no RF arcing was observed.

The presented work shows that it is possible to enclose an ICP and recycle most of the used argon. Though simple, the cleaning of the argon collected in the interface was effective even for volatile elements like Cl. As this argon was only recycled for the outer gas flow, the initial experiments indicate that no elaborate gas cleaning apparatus is necessary to avoid carryover of analytes or matrix elements.

POSTER 1 - FUN: 4

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: Jet Interface, ICP-SFMS, signal enhancement, recombination, oxide formation

Mechanism of signal enhancement in Jet Interface/ICP sector field mass spectrometer

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A latest ICP sector field mass spectrometer (ElementXR, Thermo Fisher Scientific Inc.) possesses an interface consisting of a Jet-sampler and an X-skimmer which is evacuated by using a vacuum pump with a huge exhausting volume (Jet Interface) in order to attain a higher sensitivity. In the present study effects of a vacuum pressure in the interface and geometries of sampler and skimmer on sensitivities of analytes (17 elements) and interfering polyatomic ions (analyte oxide, ArO^+, $ArNO^+$, ArN_2^+, ArO_2^+) were examined.

Vacuum pumps compared were a rotary pump with a pumping speed of 30 m^3/h (Pfeiffer Vacuum, UNO30M) named “RP” and a booster pump with a pumping speed of 130 m^3/h (Pfeiffer Vacuum, OnTool Booster150) named “BP”. Sampler cones compared were normal sampler with a hole diameter of 1.1 mmF and 6.7 mm height from bottom to the tip (following the same) and J-sampler (1.2 mmF, 8.3 mm). Skimmer cones were normal skimmer (0.80 mmF, 8.4 mm) and X-skimmer (0.80 mmF, 8.5 mm). The present study examined (1)RP/normal-normal (RP/N-N) which is a conventional interface, (2)BP/normal-normal (BP/N-N), (3)BP/normal-X (BP/N-X), and (4)BP/Jet-X (BP/J-X) which is a Jet Interface, as a combination of pump /sampler-skimmer.

The vacuum pressures measured near the interface region for four combinations of pump /sampler-skimmer (from (1) to (4)) were 1.8, 0.83, 0.83 and 0.93 mbar, respectively. Distances from the tip of sampler to a Mach disk of supersonic jet plasma, calculated from the vacuum pressure and the orifice diameter of the sampler for four combinations, were 18, 26, 26 and 27 mm, respectively, indicating that the supersonic jet became narrower and longer in the Jet Interface. This was probably due to less turbulence at the tips of sampler and/or skimmer. As a result the ion signals for analytes in the Jet Interface were more than 10 times larger than those in the conventional interface, especially those for the lighter analytes (from Li to Y). The sampling position of the supersonic jet also affected the transmission of lighter analyte ions. However a clear relationship was not found between the form of the interface and background equivalent concentrations, probably because the effect of sputtering at the surfaces of sampler or skimmer differed with the analytes. On the other hand, oxide formation ratios for the analytes as well as ion signals for $ArNO^+$ and ArO_2^+ tended to increase in the Jet Interface, suggesting a recombination of analytes and/or Ar with residual gases and/or NO^+ in the supersonic jet. In the present study both the shape of skimmer and the sampling position of the supersonic jet was further optimized for higher sensitivities of analytes. Also the effect of sputtering at the surfaces of the sampler and skimmer was investigated by LA-ICP-MS.

POSTER 1 - FUN: 5

Topics: Sample introduction and sample preparation, Plasma source fundamentals, instrumentation and mechanisms
Keywords: spray chamber, sample introduction

Evolution in Double-pass Cyclonic Spray Chamber Performance

Geoffrey Coleman[1], Brian Lato[1], Andrew Toms[2]
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Cyclonic spray chambers were introduced in the 1990s in order to improve the sensitivity as well as stabilization and washout characteristics of ICP analyses. Double-pass chambers were developed for ICP-MS in order to limit mass-loading of the plasma as well as the formation of oxides, but sacrificed a great deal of the sensitivity gain. New G3 and G4 double-pass designs demonstrate significant improvements in sensitivity compared to commonly-used chambers which have changed little over the last 10 - 15 years.

We compare the sensitivity, stabilization, and washout characteristics of the new designs primarily by ICP-OES measurements of Mn II 257.610 nm, but present sensitivity and oxide data obtained by ICP-MS, as well.

POSTER 1 - FUN: 6

Topics: Glow discharge mass spectormetry, Metrology in chemistry, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Chapman-Enskog model; Potential-energy curves; Transport cross sections; Three-temperature theory; Mobility and diffusion coefficients

Mobility of N+ ions in a helium gas by a quantal treatment of the cross sections.

Syhem Lias[1], Moncef Bouledroua[2], Kamel Alioua[3]

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This work follows recent experimental measurements of low-temperature mobility of nitrogen ions N^+ in helium performed at Tokyo Metropolitan University by the group of Pr Tanuma. More specifically, this work tries to determine theoretically the mobility in $He(1s^2)$ of ground and excited N^+ ions at low temperatures: T=4.3 and 77K. Initially, the mobilities are determined with quantum-mechanical transport cross sections without the spin-orbit effects. Then, these effects are introduced in the computation of the potential-energy curves that dissociate asymptotically into the interactions $N^+(^3P)$+He and $N^+(^1D)$+He. This PhD project will mainly focus on the behavior of the reduced mobility with the ratio E/N of the electric field and the gas density and try to explain its observed decrease near the value E/N~6Td.

POSTER 1 - FUN: 7

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: XUV, plasma, mass spectrometry, chemical imaging

Table-top XUV mass spectrometry for nano-scale chemical imaging

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Optical lasers for solid micro-sampling, coupled to mass spectrometry, e.g. laser-ablation ionization mass spectrometry imaging (MSI), have combined spatial resolution down to a few microns with extremely high chemical sensitivity. Advanced capabilities for accessing nanoscale resolution are important to investigate chemical zoning at the -interfaces. Enhanced spatial resolution implies adopting shorter lasers wavelengths [1], since the smallest spot is ~λ/2. Beyond the UV/Vis region of laboratory lasers, radiation in the XUV as found at Synchrotron and X-ray Free-Electron Lasers (XFEL), offers the sought-for capability. They permit to tune the wavelength, but it is clear that they suffer from beam-time limitation. Ideally, advanced analytical technologies should be also non-destructive. Aim of this work was to demonstrate XUV-assisted mass spectrometry for nano-scale imaging in a table-top setup in our home-lab. A pseudospark plasma XUV-source was operated which gives, about 1013 photons/(2πsr pulse) (λ between 7 nm and 16 nm) and repetition rate of up to 25 Hz. The source was operated with Ar at a pressure of 0.1 mbar and using an input voltage of 2.5 kV. The XUV radiation was delivered on Al samples using a Y/Mo-multilayer [2] that reflects about 30 % at 12 nm. A self-designed time of-flight mass spectrometer was used as detector. The TOF spectrometer had a length of 500 mm and was based in 6 electrostatic lenses and one extraction/retarding electrode, all of them independently connected to 7 bipolar high voltage power supplies, adjusted in voltages from -50 V to 500 V. A Channeltron electron multiplier with gain of about 107 at 2.5 kV was used for the time-of-flight measurements. XUV Al mass spectra show peaks for Al2+and Al+, as well as for ions originated from residual gas and metallic trace impurities. These measurements were realized without focusing the XUV beam and without destruction of the sample. In conclusion: (i) this lab-scale set up allows obtaining XUV MSI at nano-scale (ii) XUV photons are able to efficiently sample even without focusing.

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POSTER 1 - FUN: 8

Topics: Archaeometry and forensics

Keywords: TATP, DBDI, Ambient, Ionization, Peroxide

Dielectric Barrier Discharge Ionization for the Analysis of Peroxide Explosives by Mass Spectrometry

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Purpose

Triacetone triperoxide (TATP) and diacetone diperoxide (DADP) are primary high explosives mainly used in improvised explosive devices (IED) due to their easy synthesis based on readily available household chemicals. High sensitivity to shock, heat and friction makes the handling of large TATP and DADP quantities dangerous. Conventional detection methods such as UV-Vis, fluorescence, ESI/APCI-MS and GC-FID/MS are of limited value for the determination of TATP and DADP due to their chemical structure and instability. To desorb, ionize and detect TATP, DADP and structural related compounds from ambient surfaces, dielectric barrier discharge ionization-mass spectrometry (DBDI-MS) was applied.

Methods

Standard solutions of TATP, DADP, dibenzoyl peroxide and other peroxides were deposited on glass surfaces. The applied spot was allowed to dry to enhance signal intensities. The treated surfaces were subsequently measured by means of DBDI-MS. Synthesized deuterated and ^{13}C standards (TATP-d_{18}, DADP-d_{12}, DADPd_6, TATP-3,6,9^{13}C and DADP-3,6^{13}C) as well as MS/MS in a linear quadrupole ion trap were used to confirm the allocation of detected mass to charge ratios (*m*/*z*) to the respective peroxide. To quantify TATP and DADP from ambient surfaces, TATP-3,6,9^{13}C and DADP-3,6^{13}C were applied and used as internal standard. Due to the undefined residual moisture and purity of synthesized peroxides, stock solutions were quantified using quantitative nuclear magnetic resonance spectroscopy (qNMR) and DBDIMS.

Results and Conclusion

DBDI-MS spectra of TATP showed a dominant signal of *m*/*z* 240 that can be assigned to the adduct ion $[M+NH_4]^+$. The assignment was confirmed by analysis of deuterated TATP (TATP-d_{18}, *m*/*z* 258) and MS/MS experiments. In contrast to TATP, DADP was detected as *m*/*z* 182 which corresponds to the ion $[M+O+NH_4]^+$. The allocation was confirmed by measurement of DADP-d_{12} and DADP-d_6. DADP-d_{12} is detected as *m*/*z* 193 or rather $[MD+OH+NH_4]^+$, DADP-d_6 is detected as *m*/*z* 187 and *m*/*z* 188 corresponding to $[MD+OH+NH_4]^+$ and $[M+O+NH_4]^+$ respectively. Therefore DADP undergoes a covalent oxidation when ionized by means of DBDI. To investigate the stability of DADP product ion $[M+O+NH_4]^+$, DFT calculations were conducted. Analogous to TATP, dibenzoyl peroxide was detected as $[M+NH_4]^+$. Quantification of TATP and DADP from glass surfaces could be done by use of TATP3,6,9^{13}C and DADP-3,6^{13}C as internal standards over a broad concentration range. Dielectric barrier discharge ionization-mass spectrometry is suitable for desorption, ionization, detection and quantification of peroxide based explosives and related compounds from ambient surfaces.

POSTER 1 - FUN: 9

Topics: Coupling techniques (chromatography, FFF, ETV, others)
Keywords: Ambient Desorption/Ionization Mass Spectrometry, Thin-layer Chromatography

PLASMA- AND SPRAY-BASED AMBIENT DESORPTION / IONIZATION MASS SPECTROMETRY FOR QUANTITATIVE AGENT SCREENING ON TLC PLATES

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Thin-layer chromatography (TLC) is an important tool in routine analysis and active agent screening. Due to the development of stationary phases with smaller particle sizes, smaller particle size distributions, and more homogeneous film thickness it was possible to enhance the overall performance of TLC. Additionally, new commercially available stationary phases emerged with extra thin stationary phases, and larger variety of functionalized stationary phases.

At almost the same time ambient desorption/ionization (ADI) techniques emerged in 2004 and provided new possibilities for surface analysis by mass spectrometry (MS). ADI-MS ionization sources allow direct analyte desorption from a sample surface, for example, through solvent extraction or thermal heating. In a subsequent step, the desorbed molecules are ionized by the ADI probe before the ions are detected by a high resolution mass spectrometer. Early on, desorption electrospray ionization (DESI) [1] was successfully used for TLC-MS coupling [2]. So far, plasma-based ADI-sources, were barely considered for TLC-MS coupling.

In this study, established spray-based ADI-sources are compared with plasma-based ADI-sources for TLC-MS analysis. Selected plasma-based ADI-sources, namely the low-temperature plasma (LTP) [3] probe, and Flowing Atmospheric-Pressure Afterglow (FAPA) [4], are used for direct analyte desorption of natural and medical agents, and pesticides. To decrease ionization interferences, such as ion suppression by matrix components, complex sample mixtures are separated from the analytes in a previous step by the stationary phase. Additionally, a variety of different stationary phase materials are evaluated, e.g., with different layer thickness and polarity, to investigate their effect on the desorption efficiency. Lastly, a TLC-ADI-MS method is developed for quantitative analysis of selected compounds via isotope-labeled standards.

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POSTER 1 - FUN: 10

Topics: Plasma source fundamentals, instrumentation and mechanisms
Keywords: signal enhancement, nitrogen, oxygen, RF generator

Effect of molecular gases in inductively coupled plasma optical emission spectrometry: On the seeming enhancement of elements such as arsenic and selenium

Monika Winkler, Helmar Wiltsche
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The addition of molecular gases such as oxygen and nitrogen to the inductively coupled plasma (ICP) is known to increase the sensitivity of As and Se. This enhancement has been observed in both, inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS). Though this effect is routinely used, the underlying mechanism is still unsatisfactory understood, as apparent from the huge spread in the enhancement factors published.

This contribution focusses on ICP-OES, as diagnostic information from the plasma is easier accessible. It will be shown that not only As and Se are enhanced by N_2 and O_2 but also a variety of other elements with high total line energy.

By tapping the high voltage power supply of the RF generator, current and voltage fed to the power oscillator were recorded simultaneously with the emission line signal of 36 elements. It was found that even a modest addition of N_2 or O_2 increases the plate voltage of the RF generators power vacuum tube. This in turn lead to an increase of the RF power delivered to the ICP. Clearly, N_2 and O_2 alter the impedance of the plasma core causing the observed electrical effects. Depending on the quantity of molecular gas introduced into the ICP and the gas port used for addition (either intermediate gas flow or inner gas flow), the RF power level was found to increase by about 200 W.

Simultaneously with the increase of the RF power level coupled into the ICP, the plasma discharge was found to shrink. Thereby the power density in the ICP increased further.

POSTER 1 - FUN: 11

Topics: Coupling techniques (chromatography, FFF, ETV, others)

Keywords: Lithium Ion Battery, Gas Chromatography, Barrier Ionization Discharge Detector

Investigation of Lithium-Ion Battery Electrolytes by Gas Chromatography - Barrier Ionization Discharge Detector

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In recent years, lifetime and safety of lithium-ion batteries (LIBs) became more and more important for portable electric devices and automotive applications such as electric or hybrid electric vehicles.[1]

Common electrolytes in LIBs contain lithium hexafluorophosphate ($LiPF_6$) as conducting salt and a mixture of organic carbonates, e.g. diethyl carbonate (DEC) and ethylene carbonate (EC) as solvents.[2] The mixture of organic carbonates is necessary to accomplish good ion conductivity, sufficient solvation of $Li^+$and a wide working temperature range, while it is ideally electrochemically inert in a wide potential range. However, during electrochemical or thermal stress degradation reactions can occur, which is the main reason for losing the initial performance of LIBs.

A thermal or electrochemical degradation reaction leads to a variation of decomposition products, e.g. polymers, transesterfication products, fluorinated phosphates, alkylphosphates or CO_2. For the investigation of the volatile amount of decomposition products gas chromatography (GC) is a powerful tool.

During this work, the volatile decomposition products were investigated by GC - barrier ionization discharge (BID). The BID is a relatively new universally usable detector compared to the flame ionization detector (FID). It works with a 17.7 eV helium plasma that ionizes almost all compounds except neon and the plasma gas (He). The sensitivity is more than two times higher compared to FID and over 100 times higher than thermal conductivity detectors (TCD).[3]

As a part of the method development the suitability of several solvents, linearity, precision, reproducibility, limits of quantification (LOQ) and limits of detection (LOD) based on standard electrolyte and components from self-built LIBs were investigated and compared to the results of GC-MS and GC-FID.

References:

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POSTER 1 - MET: POSTER SESSION 1: Metrology

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

POSTER 1 - MET: 1

Topics: Elemental analysis, Metrology in chemistry

Keywords: Metrology, traceability, dPCR, DNA, ICPMS

Achieving metrological traceability for dPCR measurements of DNA via QQQ-ICPMS quantification of phosphorous: Advances and remaining challenges

Raquel Larios, Alexandra Whale, Jim Huggett, Alison Woolford, Heidi Goenaga-Infante

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The accurate detection and quantification of specific sequences of nucleic acids pose a great impact in several clinical applications including tumour mutation detection, pathogen resistance screening, and foetal analysis. From a metrological perspective, there is the need to develop and validate primary reference methods for DNA analysis that are traceable to the International System of units (SI).

Digital polymerase chain reaction (dPCR) is a DNA enumeration technique that does not require calibration and presents great potential in clinical diagnostic and routine testing to aid inter-laboratory reproducibility[1]. However, results provided by dPCR are not currently traceable to the SI. The ICP-MS accurate quantification of phosphorous in DNA could offer a potential orthogonal approach to validate the metrological traceability of dPCR, if molecular structures and stoichiometry are well defined.

In this work, the performance of results from dPCR have been compared with accurate ICPMS measurements of P in a pUC57 plasmid containing a portion of the human Kirsten rat sarcoma viral oncogene homolog (KRAS) gene encoding the G12D mutation. This mutation is implicated in various malignancies, including lung adenocarcinoma, mucinous adenoma and colorectal carcinoma.

Analytical challenges related to the relatively poor ionisation of P in the ICP, spectral interferences in the ICP-MS detection of this element, high procedural blanks, very low amount of sample available for repeated analyses as well as potential solutions will be discussed in this work. Those problems were overcome by using an analytical approach based on MW digestion of the sample (using micro-vessels) for subsequent analysis of the total P concentration by triple quadrupole ICP-MS in O_2 mode. The quantification was performed by external calibration using standards prepared by dilution of the reference material NIST SRM P3139a using Rh as internal standard. Quality controls standards were employed in the digestion as well as throughout the analysis procedure. The relative expanded uncertainty (k=2) for a P concentration of 23.9 mg kg^{-1} in the nucleotide was < 10 %. Moreover the DNA fragment concentration found *via* P analysis by ICP-MS was found to represent approximately 95.27% ± 7.20% of the theoretical value. Finally, the ICP-MS and dPCR values agreed well within their corresponding associated uncertainties.

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POSTER 1 - MET: 2

Topics: Metrology in chemistry

Keywords: selenium, oxidation state equilibration, isotope dilution, ICP-MS

Revisiting the Importance of Oxidation State Equilibrium of Selenium in Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

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Elements in different oxidation states may show different sensitivities in inductively coupled plasma mass spectrometry (ICP-MS). Even the results from robust isotope dilution (ID) ICP-MS can be biased if a sufficient equilibration of the oxidation states is not achieved during sample preparation. Herein, we describe the importance of the oxidation state equilibration of Se in sample preparation for ID ICP-MS for the first time. Different sensitivities of Se oxidation states were demonstrated using the isotope ratio measurements of synthetic isotope mixtures (^{78}Se and ^{82}Se) with exactly the same isotope ratio but in different oxidation state distributions. It was also shown that Se(VI) has about a 1 % higher sensitivity than Se(IV), generating bias in the isotope ratio measurements of a sample with mixed oxidation states using typical ICP-MS operating conditions. The mechanism of sensitivity difference is not clear at the moment. Non-complete equilibration of selenium species in the plasma may affect the sensitivity differences. Although it requires further study to elucidate it, the incoherent molecular formation proposed by Narukawa et al.[1] is one of the possible mechanisms. A typical microwave-assisted acid digestion procedure using HNO_3 and H_2O_2 produced Se with a mixture of oxidation states for a nutritional supplement sample. To generate a digested sample with fully equilibrated oxidation states, a modified digestion condition was developed using additional HCl as a reducing agent. It was found that the new procedure produced a digested sample containing a single Se(IV) oxidation state. The digested sample with mixed oxidation states showed approximately 1.3 % bias in the isotope ratio relative to the sample with a single oxidation state, which may result in approximately 1.6 % bias in Se quantification by ID ICP-MS. The present study revisits the importance of realizing the basic premise of ID analysis to obtain reliable analytical results, which states that a spiked isotopic internal standard should be made chemically identical to the analyte in the sample by full equilibration with proper sample preparation, and the oxidation state should be taken into account as well. Although it may not be a serious bias for most field laboratories, achieving full equilibration of the oxidation state in sample preparation for ID ICP-MS can be a significant issue when it is used to assign robust reference values for certified reference materials or proficiency testing.

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POSTER 1 - MET: 3

Topics: Metrology in chemistry

Keywords: detection, LA-ICP-MS

Mathematical aspects of detection in LA-ICP-MS

Alex Ulianov[1], Othmar Müntener[1], Urs Schaltegger[2], François Bussy[1], Niklaus Hürlimann[1,3], Federico Galster[1,4]

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Laser ablation (LA-) ICP-MS is often employed for the analysis of small isotope contents. Distinguishing between the sample signal and the background noise thus represents a routine challenge. For count numbers N_b and $N_s$collected during (equally long) background and sample measurements, respectively, the statistical significance of their net value N_s-N_b can be considered: how probable is it to obtain such values by subtracting two count numbers coming from a common statistical distribution, when N_s and N_b are measured estimates of the same mean activity [1-3]? If the corresponding one-sided probability is below a threshold, the signal is detected. Otherwise, it is not detected. The net signal value on the divide between these alternatives, given in count or mass units, is called critical value [1-5]; such values often occur in LA-ICP-MS texts [e.g., 6]. Less discussed are performances of mathematical methods, or decision rules, used to estimate them.

Here, we discuss and test decision rules available for the critical value estimation. We especially recommend using rules based on the square root transform of the count numbers [5,7-10]. The corresponding critical value for any t_b/t_s ratio at a 5% nominal rate of false detections is as follows:

$$L_c=(I_s-I_b)_c=d(1/t_b-1/t_s)+0.677(1/t_s+1/t_b)+1.645\mathrm{sqrt}[(I_bt_b+d)(1/t_s+1/t_b)/t_b]$$

where I_b and I_s, t_b and t_s denote background and signal intensities and total counting times, respectively; the value of d can be set to 3/8 or 0.4. This recommendation agrees with earlier recommendations found in texts of radioactivity monitoring, biometrics and mathematical statistics, where this formula is appreciated for its robust behaviour and relatively high power [7-9].

Using rules derived from the background standard deviation only [4], e.g., rule $L_c=2.33\mathrm{sqrt}[N_b]$ and its version for $t_b/t_s>1$ is not recommended, contrary to the past and most of the current practices of LA-ICP-MS. At small background count numbers typical of LA-ICP-MS data, using such rules results in elevated rates of false detections (background noise reported as presence of analyte in the sample).

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POSTER 1 - MET: 4

Topics: Elemental analysis, Metrology in chemistry

Keywords: Inductively coupled plasma-optical emission spectrometry; Exact matrix matching; Isotope dilution inductively coupled plasma-mass spectrometry; Infant formula; Copper; Potassium

Exact Matrix-Matching Inductively Coupled Plasma-Optical Emission Spectroscopy for the Analysis of Cu and K in Infant Formula

Sung Woo Heo, Myung-sub Han, Youngran Lim, Yong-Hyeon Yim

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The purpose of this study is to develop an exact matrix-matching inductively coupled plasma-optical emission spectroscopy (ICP-OES) as a low-cost alternative to the isotope dilution inductively coupled plasma-mass spectrometry (ID ICP-MS) method for accurate and precise measurements of essential nutrient elements K and Cu in infant formula. ICP-OES are capable of giving excellent accuracy and precision. During analysis of complex samples, ICP-OES has potential problem as biases originating from various matrix effects. The elaborated exact matrix-matching approach is demonstrated its potential to minimize biases due to matrix mismatch. The exact matrix-matching ICP-OES method was successfully validated by comparing the results with those from ID ICP-MS method. Because the approach provides reliable results, it will be an excellent choice for major elements to trace elements in a complex sample, especially when isotope dilution is not applicable due to the high spectra inteference in MS spectra or the lack of proper isotopes or the high cost of enriched isotopes.

POSTER 1 - MET: 5

Topics: Metrology in chemistry

Keywords: Isotope ratios, atomic weight, IUPAC, CIAAW

IUPAC Commission on Isotopic Abundances and Atomic Weights - CIAAW

Johanna Irrgeher[1], Thomas Prohaska[2], Michael E. Wieser[3], Thomas Walczyk[4], Juris Meija[5]

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The Commission on Isotopic Abundances and Atomic Weights (CIAAW) is an international scientific committee of the International Union of Pure and Applied Chemistry (IUPAC) under its Inorganic Chemistry Division and entrusted with periodic critical evaluation of atomic weights of elements.

Formally established in 1899, the Commission on Isotopic Abundances and Atomic Weights remains one of the oldest continuously serving scientific bodies. It was created in order to introduce uniformity in the atomic-weight values used worldwide.

Since 1970s, CIAAW evaluates other cognate data, such as the isotopic composition of elements.

Members of the Commission meet biennially where matters pertaining to the Commission's purview are discussed. The biennial CIAAW Standard Atomic Weights serve as primary source for Atomic Weight values worldwide for science, trade and also educational purposes. The tables serve as the authoritative source in science and appear worldwide on the periodic table wall charts.

Several subcommittees of CIAAW are entrusted with related topics such as isotopic abundance measurements, stable isotope reference material assessment and the natural assessment of fundamental understanding of isotopes.

Besides the Table of Standard Atomic Weights, the Commission publishes a variety of documents: Atomic Weight reports, isotopic composition reports, element-by-element reviews, technical and educational publications. All documents are also available on the CIAAW webpage (www.ciaaw.org) along with further information about commission-related topics.

In this poster the Commission, its key tasks and functions as well as current projects relevant to the mass spectrometric community are presented.

POSTER 1 - MT: POSTER SESSION 1: Metallomics

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com NORTH HALL

POSTER 1 - MT: 1

Topics: Metallomics

Keywords: Cisplatin, LC-ESI-MS, ICP-MS

IN VITRO INVESTIGATIONS ON CISPLATIN – A COMPARISON STUDY OF RESISTANT AND SENSITIVE CELLS

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Since the discovery of the antiproliferative properties of cisplatin in 1965 and its worldwide approval for clinical use in 1978, many patients with different kinds of cancers have been successfully treated. However, this platinum-(II)-based drug shows some limitations due to side effects, drug resistance and rapid inactivation leading to the investigation and development of new platinum-based drugs and other metallodrugs [1]. The resistance towards cisplatin has always been correlated to a decreased intracellular drug accumulation and/or increased drug efflux and drug inactivation by increased levels of cellular proteins containing thiol groups among other resistance mechanisms [2]. In this work we incubated cisplatin in sensitive and resistant cells of the cancer line cisA2780 and we investigated these correlations by both approaches, metabolomics and metallomics, analyzing the thiol-containing metabolites as well as the platinum intracellular content by LC-ESI-MS and ICP-MS respectively.

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POSTER 1 - MT: 2

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Metallomics, Environmental sciences
Keywords: multielement analysis, cerebrospinal fluid, flow injection

Multielement analysis in serum and cerebrospinal fluid – the combination of flow injection-ICP-tandem mass spectrometry and on-line isotope dilution

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In this work a methodology for accurate measurement of trace elements in critical biological matrices such as serum and cerebrospinal fluid has been developed. A clinically-most significant observation is expected from the analysis of cerebrospinal fluid, a sample type only available in the µL-volume range. Here the combination of ICP-MS/MS and flow injection has already proven to be a viable strategy to accurately analysing critical trace elements from µL-volume serum samples. This approach and the choice of on-line isotope dilution enables the analysis directly, without any mineralization pre-treatment, only using µL-volume samples, and is preventing proteins from raw serum from precipitating in situ. The workflow hereby presented makes a comparison between mineralization standard technique and the use of flow injection via HPLC hyphenation. The aim is to develop the clinically-best suitable method for the analysis of elements of interest such as Fe, Cu and Zn in conventionally low volumes of relevant sample types such as serum and cerebrospinal fluid.

POSTER 1 - MT: 3

Topics: Metallomics

Keywords: Nano HPLC-ICPMS, cellular glutathione peroxidase, tryptic digestion, selenocysteine, selenomethionine

Selenopeptide analysis of cellular glutathione peroxidase in mouse livers after intravenous injection of ^{82}Selenium-enriched selenomethionine

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Introduction

Selenium (Se) is one of the essential trace elements for mammals [1]. The selenoproteins including cellular glutathione peroxidase (cGPx) play a role in antioxidaion process as a scavenger of superoxide. Previously, we found that Se level in cGPx increased when administrated with selenomethionine (SeMet) than when administrated with selenite (Se(IV)) in mice [2]. Furthermore, it was suggested that SeMet replace methionine (Met) of cGPx under excess SeMet conditions. In this study, we tried to prove the replacement of Met by SeMet in cGPx at a peptide level by selenopeptide analysis using nano or capillary high-performance liquid chromatography (HPLC)-inductively coupled plasma mass spectrometry (ICPMS).

Experimental

^{82}Se, one of the stable isotopes of Se, was used for tracer experiments. Mice were injected intravenously with ^{82}Se-enriched SeMet, and the livers were collected at 6 hours after injection. Liver samples were homogenized and a soluble-protein fraction was isolated by ultra centrifugation. The soluble-protein fraction was fractionated using HPLC with a size-exclusion column and the fraction containing cGPx was collected. The cGPx standard and the collected fraction were subjected to SDS-PAGE. Gels were stained with Coomassie Brilliant Blue, and a band enriched with cGPx was cut off. Proteins were reduced by dithiothreitol and alkylated by 2-iodoacetamide and digested with trypsin in gel. Se containing peptides were detected and quantified using nano or capillary HPLC-ICPMS with a reverse-phase column [3]. Peptides were determined based on sulfur (S) concentration.

Results and Discussion

Sulfur concentrations in peptides produced by the tryptic digestion of cGPx standard were determined using nano HPLC-ICPMS. As a result, eight peptide-derived S peaks and two of peptide-derived Se peaks were detected. A strong peak of Se (defined as Se-peptide 1) was expected to correspond to the peptide with single selenocysteine residue (SeCys), while an additional weak peak (defined as Se-peptide 2) was predicted to be unexpected peptide produced by enzymatic mis-cleavage as reported previously [4]. The additional concentration of Se-peptides 1 and 2 determined based on Se data was 27.9 μM and consistent with that determined based on S data (22.3 ± 3.4 μM) within 2 σ confidential interval. This result indicated that single Se amino acid residue was contained in Se-peptide 1, attesting that the nano HPLC-ICPMS analysis combined with trypsin digestion method enables the quantification of Se containing peptides in cGPx.

The quantification of Se containing peptides in cGPx from mouse livers after intravenous injection of SeMet is now in progress.

References

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POSTER 1 - MT: 4

Topics: Metallomics

Keywords: breast cancer cells, ferritin, iron:ferritin ratios, ICP-MS, iron speciation

TOTAL AND FRACTIONATED IRON, FERRITIN CONCENTRATION AND Fe:FERRITIN RATIOS IN DIFFERENT MALIGNANCY BREAST CANCER CELL LINES: ON THE SEARCH FOR CANCER BIOMARKERS

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Iron is an essential element for cell growth and division. Recent experiments have linked a deregulation of iron's metabolism with breast cancer progression, aggressiveness and recurrence [1]. In particular, perturbations in ferritin levels (the main iron-storage protein) have shown to be associated to the progression of breast cancer towards a more malignant phenotype [2]. However, the underlying molecular mechanisms for the cancer-linked ferritin alterations remain largely unknown, since some of its functions are directly related with iron, while others may not necessarily be iron dependent. Therefore, the measurement of the Fe:ferritin ratios could be used as a complementary biomarker to the ferritin and total Fe levels to address the cell phenotype and thus, the malignancy prognosis of the specific breast cancer cells. To accomplish this aim, adequate analytical strategies for Fe:ferritin ratios accurate determinations have to be developed.

In this vein, a new analytical strategy to address total ferritin and Fe:ferritin ratios is proposed in this work for two breast cancer cell lines of different malignancy: MCF-7 and MDA-MB-231. For this purposes, two independent immunoassays (both with Fe detection by inductively coupled plasma mass spectrometry, ICP-MS) are optimized to obtain: the total ferritin content (by means of a sandwich complex using Ru-labelled antibody published [3]) and the total Fe content in the corresponding isolated ferritin (by using a biotinylated antibody and streptavidin coated magnetic beads). Such information, taken altogether with results on the total and non- ultrafiltrate cytosolic Fe concentrations obtained by ICP-MS; and the results of Fe-speciation experiments conducted by size exclusion chromatography (SEC)-ICP-MS) will be used to discuss Fe-metallomics in the context of breast cancer

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POSTER 1 - MT: 5

Topics: Sample introduction and sample preparation, Metallomics

Keywords: single cell analysis

Determination of Lead (Pb) distribution in individual Chlamydomonas reinhardtii cells by means of Single-Cell -ICP-MS

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Purpose

In order to gain a better insight into the metallome of a biological system, it is important to quantitatively determine metals in individual cells. This is needed because biological populations are heterogeneous, so it is more informative to quantitate the metal content of individual cells than obtaining average values from millions of cells that have been digested and analyzed as a single sample.

Single-Cell analysis by means of single-particle inductively coupled plasma mass spectrometry (sp -ICP-MS) is in the position to accurately determine the metal content of individual cells, transcending the limitations of other metal-detecting techniques which require specialized sample preparation, are time consuming and may sometimes be influenced by matrix effects.

In this work, the Pb content of individual *Chlamydomonas reinhardtii* cells following their incubation in different Pb concentrations is quantitated through the use of SC -ICP-MS. In addition, the ability of SC-ICP-MS to accurately measure cell culture densities is investigated. Finally, the possible effect of bioaccumulated Pb on the concentrations of endogenous cell metals, that is K^+ or Ca^+, will be investigated.

Methods

The operation of SC-ICP-MS involves the introduction of dilute cell suspensions, that is 10^4 -10^6 cells/mL, via pneumatic aspiration into a high-temperature Ar plasma. Upon entering the plasma, each aerosol droplet is evaporated and the remaining cellular material forms a solid particle which is subsequently atomized into its constituent elements. The resulting atoms are then ionized, separated by the mass analyzer and detected. Each single-cell event provides a transient signal lasting between 400-500 μs, so fast data acquisition is required. In the present study, detector dwell times from 50 μs to 10 ms were investigated. Apart from analyzing cell suspensions in a given buffer, analysis of cell suspensions following EDTA washing was also carried out so that both bioaccumulated and biosorbed Pb could be quantitated. In addition, cell suspensions are digested using microwave digestion for mass balance comparisons.

Results and Conclusions

The use of SC-ICP-MS to accurately measure cell culture densities is validated through comparisons with values obtained by using hemocytometry. Histograms of the distribution of Pb mass in cell populations are presented, demonstrating that the technique can determine Pb in the low femtogram per cell range. In addition, the determined by SC -ICP-MS average Pb mass per cell is compared with the corresponding value obtained by acid digestion and total Pb determination. This allows for assessing the SC ICP-MS technique in terms of accuracy, precision and stability. While still in its infancy, SC ICP-MS demonstrates a strong potential to contribute to the advancement of metallomics analysis.

POSTER 1 - MT: 6

Topics: Metallomics

Keywords: breast cancer, metalloproteinases, immunoassay, elemental mass spectrometry, nanoparticles

NEW STRATEGIES FOR SENSITIVE IMMUNODETECTION OF MMP-11 IN BREAST CANCER PATIENTS

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The extracellular matrix metalloproteinases (MMPs) are a family of 28 zinc-dependent endopeptidases which are involved in physiological processes, such as embryonic development, reproduction and tissue remodeling, as well as in disease processes, such as arthritis and metastasis. Based on substrate specificity and domain organization, the MMPs can be loosely divided into: collagenases (MMP-1, -8 and -13), gelatinases (MMP-2 and -9), stromelysins (MMP-3, -10 and -11), matrilysins (MMP-7 and -26), enamelysin (MMP-20), membrane-bound MMPs (MMP-14 to -17, MMP-24 and -25) and others (MMP-19, - 21, -23, -27 and -28) [1]. The main functions of this metalloproteinases are the degradation of the stromal connective tissue and basement membrane components which are key elements in tumor growth, invasion, metastasis and angiogenesis [2].

In healthy individual tissues the activity of the metalloproteinases is regulated by specific endogenous tissue inhibitors (TIMPs). However, in cancerous tissues the MMPs are overexpressed. Therefore, MMPs can be candidates as diagnostic biomarkers and functional analysis has to be designed and carried out in order to confirm their actual role in breast cancer (BC) [2].

In particular, MMP-11 (Stromelysin-3) is expressed in stromal compartment of malignant tumors and high levels of this metalloproteinase are associated with tumor progression and poor prognosis of BC. Thus, MMP-11 levels in these processes could offer a prognostic biomarker of BC.

Thus, the aim of this work is the development of new amplification strategies, based on an immunoassay coupled to ICP-MS, for highly sensitive immunodeterminations of the MMP-11 levels in serum and inflammatory cells. In this vein, an ELISA sandwich immunoassay with Au-labeled secondary antibody has been developed and the analytical characteristics of methodology have been evaluated. Finally, such application to the determination of MMP-11 in serum and inflammatory cells, from healthy and breast cancer patients, will be discussed.

References

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POSTER 1 - MT: 7

Topics: Elemental analysis, Metallomics, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Arsenic, single cell analysis, SC-ICPMS

Single cell analysis by inductively coupled plasma mass spectrometry to study the quantitative uptake of As

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It is very well known that exposure of humans to inorganic arsenic, As, in drinking water is associated with increased incidences of lung, skin and bladder cancer[i] The mechanisms by which arsenic induces this malignancy are still uncertain; however arsenic metabolites are suspected to play a pivotal role. The aim of the present study was the evaluation of As uptake capabilities at single cell level. in human adenocarcinoma alveolar epithelial cells (A549). For this purpose, we tested a novel approach, single-cell analysis by time-resolved inductively coupled plasma mass spectrometry, SC-ICP-MS/MS, for monitoring the total content of As in single cells.

The As uptake by A549 individual cells was monitored at two different arsenite concentrations, 25 and 50 µM after different exposure times to study the uptake kinetics of As into single cells. By our results using SC-ICPMS/MS we can show that the uptake of As by A549 is dependent on exposure concentration and incubation time. The total amount of As up taken per single cell was quantitatively determined by SC-ICPMS/MS. Detection limits at attogram of As were achieved by using this promising approach for the quantitative analysis of As at single cell level.

POSTER 1 - MT: 8

Topics: Metallomics

Keywords: LA-ICP-MS, gold nanoparticles, single cell analysis, integrin, inkjet printing

Quantitative Analysis of Nanoparticles and Membrane Proteins in Single Cells by Laser Ablation Inductively Coupled Plasma-Mass Spectrometry

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Previous studies generally focused on the cell colony and the obtained information was commonly the average of many cell individuals. However, each cell has a different behavior, which is known as cell heterogeneity. Single cell analysis can accurately obtain valuable information of each cell in the microenvironment and thus there is an urgent need for single cell analysis. Many methods have been successfully employed to single cell analysis, such as flow cytometry, fluorescence microscopy, capillary electrophoresis and microfluidic chips. In these methods, single cells are usually stained by a fluorescent label (e.g. fluorescein, quantum dots, green fluorescent protein, etc.) and then detected via the fluorescent signal. However, simultaneous analysis of multiple parameters in a single cell is always challenging because of the overlap in fluorescent spectrum. In addition, the linear range of the fluorescence method is relatively narrow, making difficulty for accurate quantification. To meet these challenges, a new method based on laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has emerged for single cell analysis. Dried residues of picoliter droplets ejected by a commercial inkjet printer were used to simulate matrix-matched calibration standards. Intracellular elements can be determined directly by ICP-MS at a single cell level. In combination with labeling techniques (e.g. element labeling of an antibody), biomolecules in single cells can also be determined via elements analysis by LA-ICP-MS. In this poster, an endogenous membrane protein (integrin) and exogenous gold nanoparticles (AuNPs) were chosen as proof-of-concept analytes and quantified by LA-ICP-MS. Our results demonstrate the great potential of LA-ICP-MS for single cell analysis.

Reference:

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POSTER 1 - SI: POSTER SESSION 1: Sample introduction and sample preparation

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com SOUTH HALL

POSTER 1 - SI: 1

Topics: Sample introduction and sample preparation

Keywords: SAMPLE PREPARATION, ELEMENTAL PROFILING, WINE, ICP-MS

EVALUATION OF SAMPLE PREPARATION METHODS FOR ELEMENTAL PROFILING OF WINE BY ICP-MS: COMPARISON OF DIRECT DILUTION, MICROWAVE DIGESTION, AND FILTRATION

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The elemental composition of wines can vary with respect to origin, grape variety, environment, and winemaking practices. In elemental analysis of wines, a compromise between user friendly, time efficient sample preparation methods and measurement quality must be established. Finding this balance in ICP-MS measurements of wine is challenging due to its inherently organic matrix. Undiluted direct injection of wine for ICP-MS analysis is not recommended as the variable level of organic carbon in wine requires special operating conditions and matrix-matching of carbon levels. Further, other organic matrix components (i.e. polyphenols) and suspended particulates can build up in the sample introduction system and result in variation in internal standard recovery throughout an analytical run.

Effective sample preparation techniques offer the opportunity to remove or minimize interferences, however there is no universally accepted sample preparation method for elemental profiling of wines. To that end, the effect of sample preparation method on elemental profiles of four different wines was investigated. Each wine was prepared in triplicate, using four different sample preparation approaches: Direct analysis after dilution (DD), acidification, before (AF) and after filtration (FA), and acid digestion using a microwave (MW). Matrix-matched sample preparation method blanks were included to account for any contamination from processes and materials used. Additionally, aliquots of each wine and method blank were spiked with ^{65}Cu and ^{206}Pb stable isotope standards, 100 µg/L and 5 µg/L respectively, then prepared by all four methods in triplicate to assess method accuracy and precision. In total, forty-three isotopes were monitored via matrix-matched external calibration in the range of 0.1 to 500 µg/L for each sample preparation regime. All samples were analyzed using an Agilent 8800x ICP-MS.

On average, detection limits were lower for MW treatment compared to DD, AF, and FA pretreatments. Six analytes were detected in matrix-matched method blanks of the direct methods compared to sixteen in the MW method blanks, suggesting contamination due to sample preparation. For the four wines, thirty-seven analytes differed significantly by sample preparation treatment but three were found near levels of the method blanks. Filtration methods (AF and FA) yielded significantly lower concentrations than both DD and MW for twelve isotopes in the wines. No significant difference in ^{65}Cu spike recovery was observed among the four sample preparation methods with average recoveries ranging from 91-95%, indicating adequacy of all methods to detect changes in ^{65}Cu concentration. However, significantly higher recoveries (>100%) were found for ^{206}Pb in spiked MW samples versus DD, AF, and FA treatments in which mean recoveries were 91-94%. Additionally, the suitability of measuring $^{63}Cu$and ^{65}Cu isotopes for use with isotope dilution methods in wine copper analysis is discussed.

POSTER 1 - SI: 2

Topics: Sample introduction and sample preparation, Elemental analysis, Environmental sciences
Keywords: High throughput, low sample volume

Achieving High Throughput ICP-MS Analysis with Low Sample Volumes

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Analysis of low volume samples by ICP-MS can be challenging. The application of low sample volume requirements can vary extravagently from a few ml of infant whole blood to a drop of hydrofluoric acid from vapour phase decomposition of a silicon wafer. What all low volume applications do have in common is that the sample, due to its limited availability, becomes a precious commodity.

Analytical options include diluting the sample prior to routine analysis, reducing the acquisition time to match the available volume, using low volume nebulisers and syringe driven systems capable of precise transfer of low volumes.

A number of disadvantages are apparent. Manual dilution takes time, can introduce errors and reduces the amount of analyte reaching the plasma while reducing the acquisition time has an adverse impact on the analytical figures of merit. A major concern to a busy laboratory is that the sample throughput suffers as the whole process to deal with a low volume sample takes time.

In this poster we present a 5 syringe system which allows precise delivery of low volume iron meteorite digests to a dual valve assembly. From the first valve there are options. The sample can be transfered as it is or diluted inline. The system also allows internal standard to be added if required. The second valve permits injection to allow steady state measurements or quantification by flow injection analysis. We will present the system configuation, explain the automation and present results from the high throughput analysis of the low volume iron meteorite digests.

POSTER 1 - SI: 3

Topics: Sample introduction and sample preparation

Keywords: dispersive liquid-liquid microextraction, inductively coupled plasma, flow injection analysis

Coupling dispersive liquid-liquid microextraction with inductively coupled plasma based techniques

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Dispersive liquid-liquid micro-extraction (DLLME) has been stablished as a fast and green sample preparation methodology to separate and preconcentrate analytes from complex matrices in analytical chemistry. DLLME improves limits of detection and minimizes interferences with minimum reagent volume and waste generation. Up to date, the coupling DLLME with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) has been limited mainly due to the properties of the solvents usually employed. On one hand, high volatile solvents (e.g. carbon tetrachloride) have a negative impact on plasma characteristics. On the other hand, high viscous solution could not be analyzed with the conventional liquid sample introduction system. To avoid these drawbacks, different approaches have been suggested (e.g. solvent evaporation, water back-extraction, etc.) but they counterbalance main DLLME benefits and may require complex modifications in the ICP configuration (e.g. the use of a desolvation system or oxygen addition). Due to this reasons, very few applications coupling DLLME – ICP-based techniques have been reported in the literature.

The goal of this work is to evaluate different strategies for the direct analysis of DLMME extracts with ICP-based techniques. To this end, the influence of the sample introduction system and ICP experimental conditions on analytical figures of merit have been evaluated with either high volatile (chloroform) or high viscous solvents (1-undecanol and ionic liquids). Experimental results show that direct analysis of DLLME extracts is feasible using flow injection analysis with the conventional sample introduction system. Nonetheless, high viscous solvents should be diluted before the analysis to decrease memory effects and improve sample throughput. Analytical figures of merit strongly depend on the carrier flow rate employed. Thus, when decreasing the carrier flow rate, signal strongly increases due to an improvement in the aerosol characteristics and, hence, in the solution transport rate but at the expense of sample throughput and peak resolution. Irrespective of DLLME extract properties, diluted acids could be employed as a carrier. This means that the analysis of DLLME extracts could be performed with the conventional sample introduction system.

Acknowledgements: The authors would like to thank the Generalitat Valenciana (Project GV/2014/138) and the Vice-Presidency for Research of the University of Alicante (Project GRE12-19) for the financial support of this work.

POSTER 1 - SI: 4

Topics: Sample introduction and sample preparation

Keywords: Sample Introduction; high temperature torch; Volumetric Absorptive Microsampling; Blood;

A high temperature total sample consumption system for blood analysis via ICP-MS

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This work evaluates the performance of a high temperature Torch Integrated Sample Introduction System (hTISIS) in inductively coupled plasma mass spectrometry (ICP-MS) for the multielemental analysis of whole blood. Two different quadrupole-based spectrometers were tested and the optimization studies were done with a reference whole blood material. Sample dilution factor and hTISIS temperature were taken as variables. The sample was introduced following two diverse procedures: continuous aspiration and air-segmentation. The optimum performance of the system in terms of both analytical figures of merit and accuracy was found for a 200 °C hTISIS temperature and either 1:10 or 1:25 dilution factor, depending on the ICP-MS device used. An improvement in terms of sensitivity and detection limits was obtained with the hTISIS as compared to a conventional Cyclonic spray chamber. Thus, for 1:25 diluted blood samples, hTISIS improved the sensitivity by a 2.0 to 4.5 factor. Meanwhile, the limits of detection were from 1.1 to 8.4 for the former system. This analytical parameter was in the ng L^{-1} range for the detected elements. Matrix effects in turn became less severe as the hTISIS temperature went up. All these results were obtained without a severe degradation of the plasma fundamental parameters. In fact, under optimum conditions BaO^+/Ba^+ and Ba^{++}/Ba^+ ratios were 1.2 % and 2.0 %, respectively. The method developed was applied to the analysis of low volumes (*c.a.*, 2.5 mL) of real blood samples after minimally invasive collection using Volumetric Absorptive Microsampling. The hTISIS is an easy-to-implement sample introduction system that can be employed for routine analysis through ICP-MS.

Acknowledgements

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POSTER 1 - SI: 5

Topics: Sample introduction and sample preparation, Environmental sciences
Keywords: Auto-dilution, PrepFAST, SDX, ICP-OES

Advantages of Flexible Auto-dilution Sample Introduction Solutions for ICP OES

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Purpose

Sample introduction systems play an important role in daily laboratory work. They help to streamline the analysis workflow to improve productivity. Many liquid sample handling systems based around a traditional autosampler, can now be expanded to include auto-dilution or even intelligent dilution capabilities to further simplify workflows. With these systems enabling prescriptive and intelligent, fully automated auto-dilution steps, manual dilution of standards and samples in an analytical run can be eliminated. This increases productivity, prevents re-runs of samples and reduces cost of ownership. In this poster presentation the analysis of waste waters by inductively coupled plasma optical emission spectroscopy with a fully automated, flexible sample handling system will be described.

Methods

A Thermo Scientific™ iCAP™ 7600 ICP-OES Duo equipped with the standard sample introduction kit, consisting of a concentric nebulizer, cyclonic spray chamber and 2 mm center tube was used in conjunction with the ESI prepFAST and the Teledyne CETAC™ SDX High Performance Liquid Dilution Systems. The analysis of waste water was performed according to U.S EPA Method 200.7. Both dilution systems were controlled using Thermo Scientific Qtegra™ ISDS Software that provides accessory specific plug-ins without requiring the use of external software packages.

Results

Auto-dilution systems such as the ESI prepFAST and the Teledyne CETAC™ SDX HPLD are shown to provide similar accuracy and precision to manual dilution while user interaction and the possibility for human error is reduced. With intelligent, automated auto-dilution three simple steps are required to go from stock solution to result, avoiding the time-consuming multiple preparation steps, review of acquired data and subsequent re-dilution associated with non-automated solutions.

Conclusion

With complete software control of an automated dilution system with ICP-OES, individual dilution factors can be specified for samples and standards and to intelligently dilute and reanalyze samples that fail predefined quality control limits. While eliminating the risk of contamination created by manual interaction, intelligent auto-dilution saves time, significantly improving productivity in high throughput routine laboratories.

POSTER 1 - SI: 6

Topics: Sample introduction and sample preparation

Keywords: Flow Blurring multiple nebulizer, Chemical Vapor Generation, ICP-OES, fuel analysis

Analysis of fuel samples by on-line chemical vapor generation using a Flow Blurring® multiple nebulizer in ICP-OES

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In this work, a new and simple analytical methodology based on on-line chemical vapor generation using inductively coupled plasma optical emission spectrometry for a fast and direct analysis of fuel samples is presented.

The proposed system allows analytes derivatization into the proper volatile species and so main limitations of conventional liquid sample introduction systems, as low transport efficiency, are overcome. By chemical vapor generation the analyte transport efficiency is improved and consequently, the sensitivity.

The aim of this work is to evaluate the *Flow Blurring*® multiple nebulizer [1] for the simultaneous determination of arsenic, mercury and selenium as model analytes in fuel samples (*i.e.*, gasoline and diesel samples). The nebulizer used in this study includes three independent nebulization units: one of them is used for sample or standards introduction and the remaining two are used for introducing the reagents needed for volatile species generation (*i.e.*, acid and reducing agent) [2].

Using the proposed multiple nebulizer, the chemical vapor generation reaction is easily performed directly into the spray chamber, avoiding the use of complex FIA systems, typically used for this purpose.

The proposed on-line chemical vapor generation system has been optimized using a multivariate approach. The optimization has been done in two steps: (*i*) a preliminary evaluation of all experimental factors using a Plackett-Burman factorial design, in order to know the significant ones, and (*ii*) a circumscribed central composite design to obtain the optimal experimental conditions for on-line chemical vapor generation. Under optimum conditions (total liquid flow rate: 936 $\mu L min^{-1}$, $[NaBH_4]$: 1,39% and [HCl]: 2,97 mol L^{-1}), accuracy (*i.e.*, trueness and precision) of the proposed method has been evaluated in ICP-OES by determining arsenic, mercury and selenium in spiked commercial fuel samples.

In short, it can be concluded that the use of the *Flow Blurring*® multiple nebulizer provides a simple, fast, economic and reliable alternative for direct elemental analysis of fuel samples.

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Innovation (project n. CTQ 2011-23968), and Generalitat Valenciana (Spain) (project n. PROMETEO/2013/038) for the finantial support.

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POSTER 1 - SI: 7

Topics: Sample introduction and sample preparation, Elemental analysis
Keywords: ICP-MS, Trace Analysis, High Purity Acids

Direct Analysis of High Purity Acids by Online Dilution and the Method of Standard Additions

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The majority of laboratories doing trace metal analysis require high purity acids and water to acidify, dissolve or leach samples prior to analysis. As the ability of instrumentation to detect trace metals improves, the reagents used in the sample preparation must also improve and be quantified at lower concentrations. This requires the analytical techniques used to quantify the reagents to be continuously improved.

Data will be presented for high purity nitric, hydrochloric and hydrfluoric acids analyzed directly using online dilution and the method of standard additions. The instrumentation is the prep*FAST*S from Elemental Scientific combined with the NexION 350S from Perkin Elmer.

POSTER 1 - SI: 8

Topics: Sample introduction and sample preparation, Elemental analysis
Keywords: ICP-AES, sample introductuction system, Electrospray, small amount sample analysis

Electrospray-ICP-AES for Small Amount Sample Analysis

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In recent years, target of elemental analysis has been shifted to samples of small absolute amount. For example, in the medical fields, there is growing interest in analyzing small amount of serum or organ sample to assist accurate diagnosis and making treatment plans. Inductively coupled plasma (ICP) is widely used as an ionization or excitation source for elemental analysis because of its high analytical performance. However, in conventional sample introduction system, solution sample is sprayed into the spray chamber and only fine droplets are introduced into the plasma. Therefore, sample introduction rate is not so high and so conventional introduction system is not suitable for small amount sample analysis.

In this study, a new sample introduction system was developed using electrospray method as efficient generation method of fine droplets. Electrospray method can stably generate droplets which are 1/1000 to 1/100 times smaller than conventional pneumatic spray. So, in the developed system, small amount samples can be stably sprayed and sample introduction rate was significantly improved because spray chamber does not be required. The system has a columnar structure where a metal nozzle (0.26 mm o.d. and 0.13 mm i.d.) and an exposed surface of a cylindrical electrode (14mm o.d. and 5 mm i.d.) are aligned coaxially. The distance between the nozzle and the electrode was 10 mm. This system was directly connected to the ICP torch. DC high voltage was applied between the metal nozzle and the cylindrical electrode and then charged sample was electrostatically sprayed by electrostatic force and surface tension. The charged fine droplets were drawn toward the grounded cylindrical electrode and introduced into the ICP by carrier gas flow. Oxygen and argon were used as carrier gas. Oxygen was used to prevent discharge between the nozzle and the cylindrical electrode.

Sample introduction rate was investigated by changing applied voltage and sample introduction flow rate. In investigated all conditions, sample introduction rates were higher than 75% and it showed highest rate of 95.3% at 80 µL/min. At lower sample flow rate, fine droplets were easily diffused and the sample introduction rate was reduced because many charged fine droplets were generated. On the other hand, at higher flow rate, fine droplets were not easily diffused, therefore the sample introduction rate was reduced. Compared to the conventional system, the introduction rates were much improved and the consumption of sample was reduced. So this system will be suitable for small amount sample analysis. To evaluate analytical performance of the system, calcium solution was analyzed using Ar-ICP atomic emission spectroscopy. Detailed analytical performance will be presented as well.

POSTER 1 - SI: 9

Topics: Sample introduction and sample preparation

Keywords: one-piece, nebulizer, high solids, solvents

Performance Characteristics of the OptiSolids XL High Solids Nebulizer for Analysis of Organic Materials by ICPOES

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The introduction of organic materials into an ICP has many challenges. Typical one-piece glass nebulizers have little difficulty producing a fine aerosol with organic solvents. More challenging for a nebulizer, however, is producing a long term stable aerosol with a vareity of solvents containing upwards to 10% total dissolved solids of high molecular weight polymer material. This poster will present performance characteristics of the OptiSolids XL High Solids Nebulizer (Texas Scientific Products, LLC, Argyle, TX, USA) for the determination of trace elements in organic materials by ICPOES (Prodogy 7, Teledyne Leeman Labs, Hudson, NH, USA). Organic solvents including methyl benzene and dimethylacetamide containing dissolved solids ranging from 1-10% will be presented.

POSTER 1 - SI: 10

Topics: Sample introduction and sample preparation, Elemental analysis

Keywords: Manganese dissolution, Lithium Ion Batteries, sample preparation

Method Development for Trace Elemental Analysis of Manganese in Lithium Ion Battery Electrolytes by Means of Inductively Coupled Plasma-Sector Field-Mass Spectrometry (ICP SF MS)

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The Lithium Ion Batteries (LIBs) uses lithium metal oxide cathodes ($LiMO_2$) which delivers decent capacities but suffers from fading capacity during cycling. It is reported that transition metal dissolution affects the passivation layers on graphitic anodes and originates from the acidic corrosion of hydrofluoric acid (HF) from the decomposition of the conducting salt lithium hexafluorophosphate ($LiPF_6$).[1] Furthermore, the presence of trivalent manganese ions in the structure of various cathode materials influences the structural stability as it can undergo disproportion (2 Mn^{3+} à Mn^{4+} + Mn^{2+}) resulting in divalent manganese ions which are the soluble species in electrolytes.[2,3] The understanding of transition metal dissolution during different cycling procedures and its prevention can help to increase the batteries lifetime because not only the capacity decreases with the loss of active material but it is also known that manganese is damaging the Solid Electrolyte Interphase (SEI). The SEI is built up on the anodes surface by reduction of the electrolyte in the first cycle of the battery life and protects the electrolyte from further decomposition. [4]

With Inductively Coupled Plasma-Sector Field-Mass Spectrometer, transition metal concentrations in the range of ng/g up to mg/g in the sample can be quantified. The high lithium content in the samples influences the signal intensities of several metals. Thus, the removal of most of the lithium is necessary to quantify traces of manganese in the electrolyte without high dilution of the sample.

In this work, a lithium sensitive cation exchange resin is used to suppress matrix effects induced by the high lithium concentration in battery electrolytes. The optimized method is used to investigate the manganese content in the electrolyte of cycled LNMO using synthesized cathode material *via* molten salt technique.

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POSTER 1 - SPEC: POSTER SESSION 1: Speciation

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com SOUTH HALL

POSTER 1 - SPEC: 1

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: lithium ion battery, organophosphates, high resolution ICP-MS

Analysis of organophosphates as aging products of lithium ion battery electrolytes by LC-ICP-SF-MS

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Solutions of $LiPF_6$ in organic carbonates are established as state-of-the-art electrolytes for lithium ion batteries. These mixtures are characterized by excellent cell performance and good cycling stability. The electrolytes are not chemically and electrochemically stable at elevated temperatures[1] and potentials[2] causing severe decomposition of $LiPF_6$ and the formation of numerous organophosphates[3,4], such as highly toxic dimethyl fluorophosphate (DMFP) and diethyl fluorophosphate (DEFP).

The qualitative and quantitative analysis of the organophosphates by liquid chromatography tandem mass spectrometry (LC-MS/MS) was performed in our previous work[5]. Nevertheless, the quantification with this technique was limited by strong matrix effects in aged electrolytes and a low number of commercially available standard substances. This work presents a novel liquid chromatography inductively coupled plasma sector field mass spectrometry (LC-ICP-SF-MS) method with phosphorus selective determination allowing a comprehensive analysis of the organophosphates formed in electrochemically aged lithium ion battery electrolytes.

To achieve a baseline separation of the compounds, different stationary phases were applied and compared. The most promising results were achieved with a reverse phase and a phase of hydrophilic interaction liquid chromatography (HILIC) by use of a composition of water and acetonitrile as eluent. By the hyphenation of LC with ICP-SF-MS, the parameter optimization including minimizing the introduction of acetonitrile into the plasma was performed. The most known polyatomic interferences for phosphorus were reduced by measurements in a middle resolution mode. Finally, the developed LC-ICP-SF-MS method was applied for quantification of organophosphates.

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POSTER 1 - SPEC: 2

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: Lithium Ion Battery, Gas Chromatography, Ion Chromatography, Organophosphorus Speciation

COMPLEMENTARY SPECIATION ANALYSIS OF ORGANOPHOSPHATES AS AGING PRODUCT OF LITHIUM ION BATTERY ELECTROLYTES BY MEANS OF GC-ICP-SF-MS AND 2D-IC-ICP-MS

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Since established in many both mobile and stationary applications, lithium ion batteries (LIBs) have to meet challenging demands. On the one hand, high power, high capacity and long lifetime have to be accomplished, on the other hand, safety cannot be neglected. Therefore, comprehensive knowledge of reaction mechanisms of battery components during cycling is important. Today's state-of-the-art battery systems use mixtures of cyclic and linear carbonates with a combination of lithium hexafluorophosphate ($LiPF_6$) as conductive salt. Since the salt is highly hygroscopic, traces of water in the low ppm range in the battery system are always present. The ionic form of the dissolved salt is in constant equilibrium with LiF and PF_5, the latter can undergo decomposition reactions with water and the organic carbonates eventually forming organophosphorus compounds and hydrofluoric acid (HF). These organo(fluoro)phosphates show structural similarity to chemical warfare agents (CWAs) like sarin and therefore have a supposedly high toxicity due to a similar metabolism in the human body. Even though only present in relatively low concentrations in laboratory scale cells, the quantity in mobile and stationary applications becomes significant when larger amounts of electrolyte are implemented.

In previous investigations, a large variety of organophosphates could be qualified in different electrolyte systems. A major drawback is the lack of commercially available standards for those compounds which makes quantification using molecular investigations difficult. In this study, inductively coupled plasma-mass spectrometry (ICPMS) is used to quantify the phosphorus containing molecules after separation with chromatographic techniques. Since two types - ionic and non-ionic - organophosphates are formed, the separation methods of choice were gas chromatography (GC) and two-dimensional-ion chromatography (2DIC). With these two complementary methods a complete quantification of the electrochemically formed $LiPF_6$ decomposition products could be accomplished. For identification purposes both chromatographic methods were hyphenated to molecular detectors.

POSTER 1 - SPEC: 3

Topics: Sample introduction and sample preparation, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis

Keywords: Chromium speciation, HPLC-ICPMS, dairy and cereal products, interconversion

Chromium speciation analysis in dairy products by HPLC-ICP-MS and the study of species interconversion

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Chromium (Cr) is a metal widely distributed throughout the Earth's crust. Mostly encountered chromium species in the environment are Cr(III), which has long been considered as an essential nutrient for human health, and Cr(VI) which is carcinogenic to humans. The most important contribution to the overall exposure of total chromium of the general and infant population is the food chain, particularly the dairy and cereal products. In order to assess the overall health hazard in terms of chromium in food, it is necessary to accurately determine both Cr(III) and Cr(VI) species.

This work aims firstly at the application of a previously developed method to Cr(VI) speciation analysis by HPLC-ICP-MS in 65 samples consisting of dairy and cereal products (Hernandez et al., 2017). No traces of Cr(VI) were found in all samples analyzed here. Our results are in agreement with recent studies using "on-line" speciation analysis (Novotnik et al., 2013 and 2015; Vacchina et al., 2015). In order to validate the hypothesis that chromium in food is found exclusively as Cr(III) species, a method was developed specifically for Cr(III) determination in dairy products by an experimental design. Analytical performances of the method were evaluated and the method was applied to the analysis of 17 dairy products. It is important to note that in all cases Cr(III) level balanced total chromium that was measured by using an accredited method (French comity for standardization/COFRAC) (Chevallier et al., 2015). Nevertheless, due to the relatively low number of samples quantified in this study, it is not possible to draw a general conclusion.

Finally, the interconversions of chromium species were studied by using spike standards of Cr(III) and Cr(VI) (each species was enriched in a different isotope). Our study showed that during Cr(VI) alkaline extraction, a fraction of Cr(III) was co-extracted into solution and a slight part of Cr(VI) was reduced. Therefore, the methods relying on selective extraction of Cr(VI) followed by ICP-MS determination of total chromium in the extract solution ("off-line" approaches) may lead to positively biased results in terms of Cr(VI).

It is also worth noting that the analysis of samples spiked with Cr(VI) enriched material during Cr(III) extraction showed that Cr(VI) was easily reduced to Cr(III). This may confirm the previous results in terms of lack of Cr(VI) in food as a result of the reducing features of such matrices.

POSTER 1 - SPEC: 4

Topics: Application of speciation analysis

Keywords: Inorganic arsenic, Ion chromatography, ICP-MS

Determination of inorganic arsenic in rice, paddy soil, and pore water by ion chromatography coupled with inductively coupled plasma mass spectrometry

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Chemical transformation of arsenic element can result in various chemical forms that differ considerably in properties. The toxic and biological effects of arsenic depend on the different chemical species in a sample. This study focus on the development of standardized analytical method of inorganic arsenic species in various samples. The developed method for the quantitative determination of arsenic species included the selective extraction method, the optimization of the separation and detection method and all the important instrumental and methodological parameters. The prevention of loss and transformation of arsenic species was confirmed with the developed extraction and analytical method.

Arsenic species were determined in rice that was produced in Korea, and the surrounding soil and water were analyzed to identify the source of inorganic arsenics. In a rice, the main arsenic species was As (III), and its concentration range was from 8 to 65 µg/kg. The concentrations of As (V) in a rice were in the range of 1.4 - 6.8 µg/kg. The major arsenic species was As (V) in paddy soil, and its concentration range was from 0.5 to 165 mg/kg. The concentrations of As (III) in paddy soils were in the range of 0.3 - 8.6 mg/kg. Only the inorganic arsenic species were in pore water samples. The organic arsenic species did not exist in any sample.

The concentration of As (V) is much higher than that of As (III) in paddy soil, but the concentrations of As (III) in rice and pore water were higher than that of As (V). It was described that the mobility and uptake of arsenic relyed on the arsenic species. The mobility and uptake rate of As (III) were higher than that of As(V). The high content of arsenic species in paddy soil were closely related with the total concentration of arsenic species in rice.

POSTER 1 - SPEC: 5

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: speciation analysis, lanthanides, HILIC, QqQ-ESI, LIT-ESI, spent fuel treatment processes

Development of an HILIC-ESI-MS method for lanthanides speciation in nuclear fuel treatment processes

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Research on the sustainable management of radioactive materials and wastes has led to different liquid-liquid extraction processes aiming at selectively recover targeted radionuclides from spent fuels. Radionuclide speciation analysis at various key points is essential to obtain fundamental data to better understand the mechanisms governing these treatment processes and to assess/improve their performance.

The aim of this work is to develop a speciation analysis method by hydrophilic interaction liquid chromatography (HILIC) [1] coupled to electrospray ionization - mass spectrometry (ESI-MS).

This HILIC chromatographic separation method was developed by means of synthetic samples containing lanthanides and desextraction agents: ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Columns of different geometries, packed with fully porous sub-2-µm particles (FPP) and superficially porous particles (SPP) were used to assess the best trade-off between the efficiency, the resolution, the analysis time and the waste production for each separation. The potentiality of two ESI-MS spectrometers, a triple quadrupole and a linear ion trap, to carry out the structural characterization of the lanthanide complexes will also be discussed.

Finally, the simultaneous coupling between HILIC with two mass spectrometric techniques: electrospray ionization source (ESI) and inductively coupled plasma source (ICP), implemented in glove box for a comprehensive speciation analysis will be presented.

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POSTER 1 - SPEC: 6

Topics: Application of speciation analysis

Keywords: Fluorine, ICP-MS, polyatomic ion

FLUORINE SPECIATION USING IC-ICP-MS/MS: AN APPLICATION FOR FLUORIDE AND FLUOROACETATE IN TEA

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Fluorine is one of the most reactive elements which can be found in environment, consumer products and foods such as tea. In tea, fluorine can be in ionic form of fluoride and organofluorine compound of fluoroacetate. The ionic form of fluoride is essential for promoting healthy bones and preventing tooth decay. However, it can cause detrimental effects on human such as cancer, fluorosis and low of IQ level when consumed in high amount over long periods (1). On the other hand, fluoroacetate also known as a toxic compound which can cause death (2). Until now there is no sensitive, selective and robust analytical method that able to determine fluorine and it species simultaneously except an off-line method using continuum sources molecular absorption spectrometry (CS-MAS) (3,4). Driven by these urgent demands, a method able to detect both fluoride and fluoroacetate by separation using ion chromatography (IC) and then online selectively detected using inductively coupled plasma mass spectrometry (ICP-MS) through the formation of polyatomic ion, BaF^+ was developed. The BaF^+ formation was optimized through plasma condition changes and the variation of the gases and gas mixtures in the reaction cell. The preliminary result from ICP-MS showed that total fluorine can be measured to 0.1 mg L^{-1}, while a detection limit of 1 mg F L^{-1} for fluoride and fluoroacetate could be achieved. The sensitivity is high enough to detect fluoride without interference in tea infusions without preconcentration procedures.

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POSTER 1 - SPEC: 7

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: food chemistry; milk; arsenic; speciation analysis; HPLC-ICP-MS

Ultra-Trace Speciation Analysis of Arsenic in Milk by Anion Exchange-HPLC coupled to ICP-MS

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The presence of arsenic species in foodstuff is a matter of concern at national and European level. Milk is currently one of the matrices of interest in terms of contamination with arsenic species due to its large consumption by the general population, particularly by children. Apart from the trace metals (Pb, Cd and Hg) regulated in food regulated by EU, arsenic species and particularly inorganic arsenic (AsIII+AsV) have become of interest in the last years due to their high toxicity. This also confirmed by the national French surveillance plan (2016) for inorganic arsenic in milk. At present, among all arsenic species present in food, maximum level is imposed by EU only for inorganic arsenic in rice and some rice derivatives. Therefore, obtaining occurrence data on arsenic speciation at national and European level in largely consumed foodstuff such as milk is necessary in order to assess more accurately the toxicological impact of this element. This is a challenging task given the extremely low levels of arsenic in milk (generally < 2-5 µg/kg) and the complexity of milk matrix.

This works aims at the development and validation of a method for speciation analysis of various arsenic species (including inorganic arsenic) in various types of milk by anion exchange chromatography coupled to an iCAP Q (Thermo) inductively coupled plasma mass spectrometer (AE-HPLC-ICP-MS). The extraction of arsenic species from the milk matrix was carried out using a mixture of HNO_3 1% + H_2O_2 1% in a closed microwave system. H_2O_2 is used here to oxidize As(III) to As(V) and hence to measure the entire fraction of inorganic arsenic as As(V). Species separation was carried out by using an IonPac AS7 ion exchange column (250 × 4 mm; 10 µm particles). The method was validated by means of the accuracy profile using spiked milk matrices and further applied to the analysis of the milk samples of the national French surveillance plan in 2016.

POSTER 1 - SPEC: 8

Topics: Application of speciation analysis, Environmental sciences
Keywords: arsenic, arsenolipids, environmental, toxicity

Lipophilic arsenic containing compounds in Globicephala melas (long-finned pilot whale)

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Arsenic is a ubiquitous pollutant on the trace and ultratrace level. It appears in the form of various inorganic and organic species. While legislation mostly considers inorganic arsenic due to well established methods of determination, organic species are widely overlooked.

The existence of lipophilic arsenic compounds, i.e. arsenohydrocarbons, arseno fatty acids and arsenosugarphospholipids has been known for a while now. Knowledge concerning their bioavailability, -accumulation and –synthesis remains scarce. Only recently studies have been published concerning their toxicity and bioavailability in cellular and in vivo models of hepatic cell lines and *Drosophila melanogaster* (Meyer, Matissek, et al. 2014; Meyer, Schulz, et al. 2014) showing that lipophilic arsenic can exert a similar toxicity as inorganic arsenic.

Now that the toxic capabilities have been proven, the question remains if they are of any concern for human and other life, by assessing their bioavailability and occurrence in higher lifeforms.

In this study samples from a mass stranding of *Globicephala melas* (long-finned pilot whale) have been analysed for the composition of lipophilic arsenic containing compounds and the concentrations in which they occur. These animals are highly social and stay within their pod for a lifetime, which enables accumulation studies. The focus of research lies in the comparison of brain samples with samples from other organs.

The analytical methodology makes use of parallel online-coupling of ICP- and ESI-MS to reversed phase HPLC which allows for quantification and identification of the compounds of interest simultaneously (Amayo et al. 2011). Results are validated and compared using a traditional microwave digestion based method.

It could be shown that the expression patterns of arsenolipids occurring in the brain a vastly different from the ones occurring in any other organ. In addition, the ratio between lipophilic and water soluble arsenic in the liver was shown to be constant throughout the animals live whereas it shifts towards lipophilic arsenic in the brain of the animals. The nature of these compounds occurring only in the brains of *Globicephala melas* is investigated.

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POSTER 1 - SPEC: 9

Topics: Sample introduction and sample preparation, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis

Keywords: Selenium, yeast, SeCys

Method development for quantification of selenocysteine in yeast samples by HPLC-ICP MS

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Selenium-enriched yeast is a popular food supplement and an established ingredient of Se-enriched premixes and finished feed products. The emerging use of the Se-yeast and its extracts for cultivating mammalian cell cultures and altering cell functions for therapeutic applications was also reported [1]. The understanding and optimization of the biochemical processes of Se incorporation during yeast growth and the characterization of the final products requested by regulatory agencies require the development of suitable methods for speciation analysis [2].

Most of the methodological developments concerning the analysis of selenized yeast have been focused on the quantitative determination of selenomethionine (SeMet) believed to be the only selenoanimo acid produced by yeast as it does not have the selenocysteine insertion (UGA) codon. These efforts culminated at the issue of a certified reference material (SELM-1) and resulted in the acceptance of the SeMet content as an indispensable parameter of the quality control of marketed products.

The other mainstream of analytical chemistry developments included the identification of the myriad of selenium metabolites allowing the quasi-complete characterisation of the water soluble part of the Se yeast metabolome.

However, so far, the mass balance of selenium species has been never reaching 100% in comparison with the total Se content suggesting the presence of unaccounted for selenium species lost during standard analytical procedures. At the same time, the recent study demonstrated that - despite of absence of UGA codon - selenocysteine (SeCys) can be produced by yeast [3].

The contribution discusses the systematic development of an analytical method for quantification of selenocysteine in Se-rich yeast. The study is complemented by the description of the reactivity of Se-species during derivatization by carbamidomethylation by electrospray MS^2 after custom-designed 2D HPLC purification using ICP MS monitoring.

References

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POSTER 1 - SPEC: 10

Topics: Application of speciation analysis

Keywords: enriched pea sprouts, selenium compounds, iodine

Stability of selenium compounds in enriched pea sprouts

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Selenium and iodine are essential trace elements for human and animals health. Slovenia is known as a country with low selenium content in soil (up to 0.7 µg/g) and consequently also food contains low amounts of selenium. To avoid health problems caused by selenium and iodine deficiency, other sources of these two elements should be found. Selenium and/or iodine enriched cultivated plants could be an effective way to improve food quality and to provide sufficient intake of these elements for humans. Selenium compounds in pea sprouts from seeds soaked in solution of Se(IV) or Se(VI) (10 mg/L) alone or in combination with I(–I) or I(V) (1000 mg/L) were investigated.

After extraction with non-specific enzyme Protease XIV, separation and identification of Se compounds in pea sprouts by HPLC-ICP-MS were made. Seperation of SeMet, $SeCys_2$, Se(IV), Se(VI) was performed in two anion exchange coloumns: Hamilton PRP-X100 (250 x 4.1 mm ID) and Thermo IonPac AS11 (250 x 4 mm ID), with different mobile phases. In addition, affinity (HiTrap Heparin 5 mL) and size exclusion columns (TSK 55 S HW (600 x 10 mm) and TSK 40 S SW (250 x 8 mm)) were used.

In all pea sprout encymatic extracts, SeMet and Se(VI) were identified with both anion exchange columns, while Se(IV) were found only after separation on Hamilton PRP-X100. Se(IV) could be oxidized in powder sprouts to Se(VI), because the encymatic extractions were not made at the same time, the time difference was one and a half year. From the same extract as separation on Thermo IonPac AS11 collumn was done, with the size exclusion chromatography SeMet and Se(VI) were found. With affinity chromatography GPx and SePP were not identified.

To conclude, iodine in different forms in soaking solutions did not affect on Se compounds determination in pea sprouts.

POSTER 1 - SPEC: 11

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: Speciation, HPLC, ICP-MS, Drinking water, Toxic elements

Speciation of As, Cr and Sb in bottled water samples using hyphenated technique HPLC/ICP-DRC-MS

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Water is an essential component of the human nutrition. It maintains bodily functions, carries nutrients to cells and helps you hydrate your body. In recent years sales of bottled drinking water is rising sharply and bottled water can be found everywhere around us. The effect of arsenic, chromium and antimony on human body strongly depend on chemical forms in which they occur. Cr^{VI} is well known as a human carcinogen while Cr^{III} does not exhibit adverse effects on the human body. In case of arsenic and antimony, their trivalent species are much more toxic than pentavalent. Arsenic trioxide has been classified as human carcinogen while complex organic arsenic compounds are not harmful to humans. Considering that quality control of bottled water destined for human consumption should not only focus on total element concentration but also determination of As, Cr and Sb species concentration. High performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC/ICP-DRC-MS) is currently the most frequently used hyphenated technique in the field of speciation analysis.

The main goal of the presented study was to extend the applicability of previously developed in our laboratory method for the multielemental speciation analysis of five toxic species: As^{III}, As^{V}, Cr^{VI}, Sb^{III} and Sb^{V} in drinking water by HPLC/ICP-DRC-MS. This procedure allowed to examine the samples characterized by mineralization up to 650 mg L^{-1}, and used the external calibration method. Scope of the procedure was extended to maintain samples characterized by mineralization up to 7000 mg L^{-1}. In order to achieve that we had to develop a new calibration method which allowed to reduce matrix effects affecting measurements in high mineralization samples. Two point standard addition calibration method was chosen as optimal. Beyond procedure applicability extension research were focused on evaluation of impact of the material and color of the container (green, blue or pink; glass or PET – polyethylene terephthalate bottles) and the type of stored water (carbonated and non-carbonated) on the concentration of mentioned above toxic As, Cr and Sb species.

All measurement were conducted using Elan DRC II ICP-MS instrument (PerkinElmerSCIEX, Ontario, Canada) in DRC mode (with oxygen as reaction gas) coupled to HPLC system consisted of a PerkinElmer Series 200 pump and column oven and an PerkinElmer Series 225 auto sampler equipped with a Peltier Cooling Tray and a stainless steel injection needle with a 100 µL sample loop (PerkinElmerSCIEX, Ontario, Canada). PRP-X100 anion-exchange column (Hamilton, Bonaduz, Switzerland) was used execute the separation of mentioned above species.

[1] B. Markiewicz, I. Komorowicz, D. Barałkiewicz, Talanta 152 (2016) 489–497.
[2] M. Marcinkowska, I. Komorowicz, D. Barałkiewicz, Talanta 144 (2015) 233–240.
[3] I. Komorowicz, D. Barałkiewicz, Talanta 84 (2011) 247–261.

POSTER 1 - SPEC: 12

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: ICP-MS, identification, speciation

The multi-methodical application of using ICP-MS in combination with off-line thermal desorption GC-MS and direct-inlet MS for the identification of organometallic substances

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In polymer applications organometallic additives are widely used, however, when dealing with consumer goods, in many cases the history of the sample is unknown and the distributor want to get full knowledge of the used additives including the organometallic compounds. By ICP-MS inorganic analysis is done in order to detect the suspected elemental content, while thermal desorption GC-MS or direct in-source desorption (direct-inlet) MS might be used for the identification of the organic/organometallic content. The use of thermal desorption GC-MS has its advantage that it allows identification of (semi-)volatiles directly from polymer matrixes where mostly parts of the organometallic compounds are detected. As an alternative, direct-inlet MS can be used which requires the introduction of the sample directly into the ion source of the MS by a probe introduction system and a vacuum port. The sample gets evolved by sequential heating of the sample probe and utilizing the presented vacuum in the MS. The evaporated analytes are immediately ionized by deflected and accelerated into the ion optics. For this study certain samples were selected for the evaluation of their organometallic composition. In all cases organometallic content was presumed as some elements like Zn, Cu and Sn surprisingly appeared. Due to the difference in sample matrixes and the different physical-chemical character of the target analytes different analytical and sample preparation methods were applied. As a first example, in a blue polyvinylbutyral sample used in the automotive industry unknown blue coloured pigments were detected by optical microscopy. The elemental content was measured by ICP-MS resulting in a major signal of copper. After a sample clean-up and precipitation step the pigments were isolated from the polymer and identified by direct-inlet MS being dichlorinated phtalocyanine-type coordination complex of copper. A second sample was an EPDM rubber containing a higher concentration of zinc. Higher concentrations of zinc might be feasible if ZnO or zinc stearate was used, however identification by thermal desorption GC-MS was required in order to specify the presence of other Zn containing substances, as alkyl dithiophosphates, mercaptobenzimidazoles, mercaptobenzothiazoles and alkyl dithiocarbamates are also frequently used. In this sample zinc bis(dibutyldithiophosphate) has been confirmed by thermal desorption GC-MS. A next sample non-plasticized PVC used as food storage container did gave a high Sn content. By thermal desorption GC-MS organotin compounds based on bismercaptoacetic acid 2-ethylhexyl ester di methyltin could be confirmed. The combination of several mass spectral methods is able to characterize unknown organometallic substances in polymers.

POSTER 1 - SPEC: 13

Topics: Sample introduction and sample preparation, Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: Arsenic, speciation, rice, food, hydride

Testing for maximum levels of inorganic arsenic in rice via hydride generation ICP-MS

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Commission regulation (EU) 2015/1006 established maximum levels for inorganic arsenic in rice of 0.20 mg/kg for milled rice, 0.25 mg/kg for parboiled rice, 0.30 mg/kg for rice waffles, rice wafers, rice crackers and rice cakes, and 0.10 mg/kg for rice destined for the production of food for infants and young children.

Measurement of total arsenic in rice by ICP-MS can be performed by ICP-MS simultaneously with Pb and Cd analysis, as required under Commission Regulation (EC) No 333/2007, and is often sufficient to establish whether inorganic arsenic can exceed the maximum levels. Where total arsenic exceeds the inorganic arsenic level there is a need for rapid, low cost specific determination of inorganic arsenic (As(III) plus As(V)).

Musil et al. (2014)* demonstrated the application of species-specific hydride generation ICP-MS for inorganic arsenic determination in rice using high (5M) hydrochloric acid concentration and (non-hydride forming) Rh internal standardisation introduced online following hydride generation (and thus using wet-plasma conditions). There are substantial benefits, however, to introducing an internal standard at the earliest possible stage in the analytical procedure. Addition of internal standard (via calibrated pipette) at the sample weighing stage adjusts for variation during extraction, dilution, hydride generation and ICP-MS measurement.

We demonstrate application of hydride forming internal standardisation using the hydrideICP (Elemental Scientific, Omaha, NE) accessory coupled to NexION ICP-MS (PerkinElmer, Shelton, CT, USA) at high hydrochloric acid concentration through spike recovery and analysis of reference materials. Furthermore, we explore the use of species-specific pre-reduction allowing operation of hydride generation at lower hydrochloric acid concentrations, providing benefits in specific hydride generation, internal standard usage, and health & safety requirements within a commercial laboratory setting.

* Musil et al., Speciation without Chromatography Using Selective Hydride Generation: Inorganic Arsenic in Rice and Samples of Marine Origin. Anal. Chem. 2014, 86, 993−999.

POSTER 1 - SPEC: 14

Topics: Sample introduction and sample preparation, Application of speciation analysis
Keywords: ultrasonic standing waves, ICP-OES, disperse particle extraction

On-line fractionation of aqueous samples using acoustic standing wave particle manipulation with ICP-OES

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ICP-OES is a well established method for identification and quantification of elements in solid and aqueous samples. However, without using it in combination with a hyphenated separation technique it is lacking information about the chemical nature of the element in the sample.

In this work we present a newly developed method enabeling online fractionation of aqueous samples with a disperse particle extraction (DPE) approach. Commercially available, as well as self-synthesized surface modified particles have been applied on aqueous samples in order to separate the organic-complexed fractions from the free ionic fraction of selected analytes. The surface modified particles are added to the sample and thoroughly mixed. The suspension is then introduced to the fractionation system, where the particles are separated from the sample and the fraction of the sample which did not bind to the particles passes directly to the ICP-OES. Acoustic standing waves are used to excert a trapping force on the patricles within a commercial flow-through-cell, thus serparating them from the sample suspension and releasing them after it has passed the cell. The implementation of this separation cell removes the centrifugation step from the conventional DPE method, therefore making it automatable and suitable for on-line applications.

POSTER 1 - SPEC: 15

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Environmental sciences
Keywords: ICM ICP-MS/MS, Gadolinium, Speciation

Development of an HPLC-ICP-MS method for the speciation analysis of different contrast agents in environmental samples

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In recent decades, surveillance and protection of the aquatic environment has been steadily

improved to ensure a good overall chemical condition of different water bodies such as river systems, eastuaries or coastal waters.

In addition to the “classical” monitoring of the physical and microbiological water quality, attention has increasingly focused on the investigation of either new organic contaminants, as well as trace elements and their species. Beside the well investigated speciation of elements such as Tin, Arsenic, Mercury or Chromium little is known about the potential impact of new elemental species such as nano materials or contrast agents.

In particular Iodinated as well as Gadolinium based contrast agents are frequently used pharmaceuticals, which are used to improve the visibility of internal tissue structures during computed tomography (CT) and MRT.

These contrast media are applied in high amounts and are excreted in unmetabolized form within hours via the renal system. Due to their special chemical properties they are not retained by classical waste water treatment, which allows them to enter the aquatic environment. While considered harmless to the human body, their overall long-term effects on the aquatic environment are still unknown.

In particular iodinated contrast agents such as Iopromide or Iohexol are used in the ton per year range, hence monitoring their distribution e.g. in the German rivers has become a task of utter most importance. Ecotoxicological information about these species is limited and although they show only negligible effects on marine life, the fate of their metabolites and by-products is still largely unknown and requires further investigation.

Within this background this contribution focused on the improvement of a separation method for selected contrast agents using HPLC hyphenated with ICP-MS to allow their accurate quantification at lowest concentrations. Therefore different parameters such as instrumental settings, column type or mobile phase composition have been examined to allow a highly resolved separation of the targeted species. In addition, the application of ICP-MS/MS has been tested to improve the element specific detection of the analysed species.

POSTER 1 - SPEC: 16

Topics: Environmental sciences

Keywords: iodine, drinking water, raw water, speciation analysis, ICPMS

Speciation analysis of iodine in drinking water and raw water using IC-ICPMS and SEC-ICPMS

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Introduction

Iodine is an essential element for human as a constituent of thyroid hormone. Iodine cycles in the environment and flows into river water by rainfall. River water is used as source of drinking water in public water treatment plants, and iodine is contained in drinking water as iodide and iodate. Previously, it was reported that toxic disinfection by-products (DBPs) containing iodine are potentially generated during the water disinfection process [1]. The toxicity of those iodinated DBPs significantly higher than that of the chlorinated and brominated analogues [1], and thereby it is important to analyze the chemical forms of iodine in drinking water and raw water in terms of public health and safety. In this research, we tried to reveal the environmental behavior of iodine by speciation analysis of iodine in drinking water and raw water using ion chromatography (IC)-inductively coupled plasma mass spectrometry (ICPMS) and size exclusion chromatography (SEC)-ICPMS.

Experimental

The drinking water, which was ozonated and chlorinated in the water treatment plant, was sampled in Chuo University in Tokyo, and the raw water was sampled in Arakawa River. The raw water sample was filtrated with a 0.45 μm nitrocellulose filter. Total concentration of iodine was determined using ICPMS, and the speciation analysis of iodine was conducted using IC-ICPMS and SEC-ICPMS. In total iodine analysis, tetramethyl ammonium hydroxide was used to adjust the pH of samples to 12. An anion exchange column was used for IC with KOH eluent, and 20 mM Tris-HNO_3 containing 0.3 wt% ethanol at pH 8 was used as an elution buffer for SEC.

Results and Discussion

Iodide and iodate were detected in both the drinking water and the raw water. Besides, iohexol and iopamidol were detected in both the drinking water and the raw water, and diatrizoic acid was additionally detected in the raw water. In the drinking water, the recovery rate of iodine (the sum of iodine compounds concentrations detected with IC-ICPMS / total iodine concentration) was approximately 100%. In contrast, the recovery rate of iodine was 35% in the raw water, suggesting that the other 65% was accounted by non-anionic iodine compounds that are not eluted with KOH. We then employed SEC-ICPMS for speciation analysis of iodine in the raw water. As a result, unknown iodine compounds that were undetectable with IC-ICPMS, were found in the raw water. It was thought that those unknown iodine compounds were humic substances with high molecular weight. Furthermore, from the analysis of fulvic acid standard using SEC-ICPMS, the peaks of unknown iodine compounds in the raw water showed the same retention time as the peaks of putative iodine-fulvic acid complexes, suggesting that iodine exists as humic compounds in the raw water.

References

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POSTER 1 - SPEC: 17

Topics: Coupling techniques (chromatography, FFF, ETV, others)
Keywords: Tin, Speciation, TBT, Resolution, Sector

High Sensitivity Tin Speciation Using a New GC Interface with Sector Field High Resolution ICP-MS

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Often the total elemental concentration of an analyte is not sufficient to accurately assess its impact on the environment or human health. That is because toxicity and mobility are dependent on the species of the analyte. Tin, for example, can be found in a variety of molecules, each with different degrees of toxicity and persistence. Tributyltin (TBT) is widespread in the environment due to its mobile and persistent nature. As TBT is toxic at very low concentrations, there are strict legislative limits (e.g. the European Water Framework Directive).

This presentation shows the use of a new GC interface together with Sector Field ICP-MS for sensitive compound-specific quantification of tin species. This interface can be quickly and easily installed. By means of the flexible and light design of the heated transfer line, the ICP-MS torch position can be easily tuned without being affected by the weight of the interface. We show how a stable temperature profile and the absence of cold spots avoids condensation and peak broadening.

Because of the high acceleration voltage of Sector Field ICP-MS this technique is extremely sensitive. In combination with its low backgrounds, this leads to the low detection limits required for sensitive tin speciation analysis.

POSTER 1 - SPEC: 18

Topics: Application of speciation analysis, Environmental sciences, Metrology in chemistry
Keywords: mercury speciation, biota, isotope dilution, Specimen Bank

Collaborative study on mercury and methylmercury quantification in fish samples from the German Environmental Specimen Bank

Paola Fisicaro[1], Emilia Vasileva[2], Ina Fettig[3], Jan Koschorreck[3], Christian Piechotta[4], Caroline Oster[1], Enrica Alasonati[1], Maria Estela Del Castillo Busto[1], Sabine Azemard[2]

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Mercury in its many chemical forms is highly toxic to human, animal and environmental health. Its ability to accumulate in terrestrial and aquatic biosystems makes it a particularly insidious threat to environmental sustainability. The assessment of the ongoing effect of mercury on humans and the environment remains of high importance and is critically dependent on accurate measurements to assess concentrations and trends.

The aim of this work is to present the results of a collaborative study conducted on fish samples collected in collaboration with the German Environmental Specimen Bank. Fish samples of bream, roach and pike were freeze dried, cryo milled, homogenized and sub-sampled.

Robust measurement procedures for inorganic and methylmercury quantification in fish have been developed. The procedures are based on liquid-liquid extraction, using ethylation as the derivatisation step and isotope dilution (ID) ICP-MS. Methods have been validated using certified reference materials (CRMs) with different origin, fat content and mercury level as IAEA-407 (fish tissues without fat), NIST-1947 (fish fillet, 8% of fat) and NRC-DOLT-4 (dogfish liver). The values found for total Hg and for MeHg were in great agreement with the certified values.

These validated measurement procedures were applied to quantify the total mercury and the species in different types of fish samples. It was observed a good agreement between the sum of IHg and MeHg measured and the total Hg content measured. No heterogeneity among the different samples was observed. A tendency for demethylation of MeHg occurring when samples were γ-irradiated, was observed by GC-ID-ICPMS. However, the trend was not significant with respect to the method uncertainties.

POSTER 1 - VENDORS I: POSTER SESSION 1: Vendors I

Time: Tuesday, 21/Feb/2017: 2:00pm - 3:40pm

Location: ARLBERG-well.com FOYER

POSTER 1 - VENDORS I: 1

Poster presentation (vendor paper)

Topics: Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: ICP-MS, HPLC, Arsenic, Speciation, Pharmaceutical

Speciation of Arsenic in pharmaceutical products using HPLC-ICP-MS

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The level of potentially harmful substances – including inorganic contaminants – in pharmaceutical products is subject to regulatory control in many countries. The latest revision of the US Pharmacopeial Convention (USP) General Chapter <232>, and the International Conference on Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH) Q3D require medicines to be assessed for a wider range of “Elemental Impurities”, many of which must be controlled at lower level that required under the previous regulations. This change has increased the demand for trace elemental analysis in the pharmaceutical industry.

Of the 20 or so elements mentioned in the new methods, some have potential toxicity that is highly dependent on the chemical form of the element. Of particular interest are arsenic (As) and mercury (Hg), where the inorganic and organic forms have vastly different toxicity. It is relatively unlikely that the most toxic (organic) forms of Hg would be present in most pharmaceutical products. But the most toxic (inorganic) forms of As occur naturally and have been widely used as biocides, and may therefore be present in some of the natural materials used in pharmaceutical manufacturing. The new elemental impurity methods suggest that speciation analysis is an appropriate method for determining whether arsenic is present as the inorganic (As(III) and As(V)) or organic forms if the total As concentration found exceeds the defined maximum limit.

This work describes a robust speciation method, using high-performance liquid chromatography coupled to inductively coupled plasma-mass spectrometry (HPLC-ICP-MS), for the routine speciation of five arsenic compounds in pharmaceutical products. The validation of the method was done following the methods defined in the pharmacopeias.

Poster presentation (vendor paper)

Topics: Elemental analysis, Coupling techniques (chromatography, FFF, ETV, others), Application of speciation analysis
Keywords: ICP-QQQ, metals, organic solvent, Gel Permation Chromatography

Investigation of the potential of the ICP-QQQ for the quantification of metals in organic solvents and LC-ICP-QQQ for separation of metal complexes by GPC

Charles-Philippe Lienemann[1], Alain Desprez[2], Sylvain Carbonneaux[1], Fabien Chainet[1], Frédérique Bessueille[3], Marie-Laure Milliand[3]

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In recent years, the petroleum industry has become increasingly interested in the determination of trace and ultra-trace metal levels in crude oil and petroleum products. Established and emerging applications include controlling contamination during refining, monitoring the levels of catalyst poison elements in process streams, using trace element levels, metal porphyrins and other complexes as geochemical biomarkers, and identifying and reducing the sources of atmospheric and environmental pollution from fuels.

Because of its high sensitivity and simple mass spectra, quadrupole ICP-MS (ICP-QMS) is able to achieve sufficiently low detection limits for the elements of interest in the industry. However, the analysis of organic samples by ICP-MS requires a specific sample introduction configuration, and the high carbon and oxygen content in the plasma gives rise to several intense carbon-based polyatomic interferences.

Agilent's 8800 triple quadrupole ICP-MS (ICP-QQQ) offers a unique capability for interference removal, using controlled reactions in the collision/reaction cell. This provides an interesting alternative to ICP-QMS to solve the polyatomic interferences and achieve lower detection limits and more reliable quantification for key analytes in organic solvents.

Experiments were performed using a sample introduction system adapted for organic samples. Solvent-resistant peri-pump tubings, O2 addition to the plasma, platinum cones and lower temperature in the spray chamber were used to perform both total metal quantification and LC coupling for the separation of metal-organic aggregates using Gel Permeation Chromatography (GPC), also referred to as Size Exclusion Chromatography (SEC).

As the S, V and Ni containing aggregates are targeted to be eliminated as much as possible during before hydrocracking processes, the size speciation gives a valuable information on the selectivity of the catalysts used metal removal in order to improve the refining yield.

POSTER 1 - VENDORS I: 3

Poster presentation (vendor paper)

Topics: Coupling techniques (chromatography, FFF, ETV, others)

Keywords: Speciation, software, legislation

Advanced software solutions for integrated elemental speciation by IC, LC and GC coupled to ICP-MS

Julian David Wills, Daniel Kutscher, Shona McSheehy Ducos, Antonella Guzzonato

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Purpose

International and national regulatory bodies continue to expand their analytical requirements beyond simple total element quantification to include species specific quantification. This evolution can be seen in updated methods and guidance in environmental[1] and food[2] applications. This represents a significant challenge in both routine and research laboratories where, in addition to adopting new hardware to meet the requirement for elemental speciation (ion chromatography for example), existing users are required to learn the accompanying new software packages.

Methods

A range of Thermo Scientific™ speciation devices (including IC, LC and GC) were coupled with Thermo Scientific™ iCAP Q and Qnova Series ICP-MS systems to perform elemental speciation measurements. A new software plug-in, ChromControl, for the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used to interface the ICP-MS with chromatographic systems running the Thermo Scientific™ Chromeleon™ Standard Instrument Interface (SII).

Results

In this poster presentation, examples will be shown for routine and advanced applications of IC, LC and GC coupled to ICP-MS through the implementation of a single analytical workflow, independent of the type of speciation device used.

Conclusions

Through the implementation of advanced software, workflows in elemental speciation are identical to those in total element quantification, facilitating the adoption of these new techniques in laboratories.

References:

1. 1. European Water Framework Directive homepage; http://ec.europa.eu/environment/water/water-framework/index_en.html
2. 2. US Food and Drug Administration (FDA) Elemental Analysis Manual (EAM) for Food and Related Products homepage: http://www.fda.gov/Food/FoodScienceResearch/LaboratoryMethods/ucm2006954.htm

POSTER 1 - VENDORS I: 4

Poster presentation (vendor paper)

Topics: Application of speciation analysis

Keywords: chromium, speciation, IC-ICP-MS

Chromium speciation analysis by IC-ICP-MS under Empower software

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Speciation analysis for chromium is increasingly becoming a regulatory requirement to assess the quality of drinking water. With the public health goal in California set to just 20 ng/L Cr(VI), the sensitivity of the technique and accuracy at low levels become increasingly important. One of the most sensitive analysis techniques for this task is IC-ICP-MS. Systems with a metal- free flow path are one option to guarantee inertness and to achieve low backgrounds for the benefit of low-level analysis. In addition, software which can operate and control the entire speciation system advances productivity and ease of use. Here we report data on a new speciation method based on anion exchange using a Metrohm 940 Professional IC Vario One with Metrohm 858 Professional Sample Processor coupled to a PerkinElmer NexION 350D ICP-MS. The complete system is run under Empower3 software.

In order to determine both Cr(III) and Cr(VI), water samples were treated with EDTA at elevated temperature to complex Cr3. Tests were carried with a variety of water samples which showed the need to adjust the EDTA concentration to ensure complete complexation. Using a MetroSep Carb 2 column under optimized eluent conditions resulted in a high resolving power for the separation of Cr(III) and Cr(VI) within a run time of 10 min. Calibrations were carried out from 10 ng/L to 10 µg/L , showing very good linearity (r^2 values > 0.9999) and samples were measured down to low ng/L range. The relatively small injection volume (20 µL) contributes to the observed robustness of the chromatography.

POSTER 1 - VENDORS I: 5

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: Extractables and Leachables

Current Trends, Analytical Workflows and a Case Study in Extractables and Leachables Analysis, combining LC/MS, GC/MS and ICP-MS data analysis

Paige Elana Solomon, Jenny Nelson

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Highly publicized incidents and stricter regulatory controls have put a sharper focus on the analysis of contaminants in pharmaceutical products and medical devices, whether they are derived from raw materials, introduced during manufacturing, or from extractables and leachables (E&Ls) that are transferred to the drug product from packaging or container closure systems (CCS). The advent of single use bioprocess systems in bio-therapeutics manufacturing has introduced a new potential source for E&Ls as these systems often comprise polymer components.

We will discuss current trends in E&L analysis including changes to the regulatory landscape, and we present an overview of analytical technologies available for E&L analysis. We include case studies in the analysis of E&Ls with a highlight on a model single use bioprocess system. A variety of analytical technologies and workflows were used for initial screening of the extracts for a holistic understanding of the samples, followed by a more specific analysis by ICP-MS, LC/MS and GC/MS for detecting, identifying and quantifying elemental, volatile, semi-volatile and non-volatile compounds in the E&L extracts.

POSTER 1 - VENDORS I: 6

Poster presentation (vendor paper)

Topics: Elemental analysis, Environmental sciences

Keywords: ICP-MS, HMI, Aerosol Dilution, Seawater, Loop Injection

Direct, Rapid Analysis of Undiluted Seawater using ICP-MS with an Aerosol Dilution System

Glenn David Woods[1], Shaun Fletcher[2]

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The analysis of seawater presents numerous analytical challenges – the typical elemental targets are at low concentrations and the seawater matrix concentration usually precludes direct measurement by ICP-MS. Approaches usually involve some form of matrix elimination either by liquid-liquid or solid liquid matrix elimination and preconcentration. Whilst these approached usually work for the majority of elements, they tend to be time consuming, expensive and require user expertise.

With the greater sensitivity of modern ICP-MS instrumentation a simple dilution approach can often be used to reduce the total dissolved solids (TDS) levels typical of seawater (~3%) to that more compatible to ICP-MS (~0.2-0.3%). Usually, a 1:10 or 1:15 dilution is used and whilst this can work well there is a possibility of introducing contamination from the diluent and/or making an error during the dilution step; additionally, the preparation step requires time and a degree of expertise.

An alternative approach is to use so-called “aerosol dilution” whereby the matrix loading within the plasma is reduced in the aerosol phase - in effect diluted using clean, dry argon. This “High Matrix Introduction” (HMI) system is demonstrated with loop injection for the application of direct, undiluted seawater analysis by ICP-MS.

POSTER 1 - VENDORS I: 7

Poster presentation (vendor paper)

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: ICP-QQQ, MS/MS, Abundance Sensitivity, ICP-MS, Organic Solvent, Biofluids, Nuclear

Practical Benefits of Abundance Sensitivity Using ICP-QQQ

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Abundance sensitivity is a measure of the contribution from a large matrix mass peak next to the target analyte mass peak. The abundance sensitivity for quadrupole based instrumentation can typically be around $5x10^{-7}$ to $1x10^{-7}$ and higher in Sector Field systems (although this can partially be compensated for by increasing resolution) – it is essentially the measure of peak tailing from the matrix element peak.

This poster will demonstrate the improvement in abundance sensitivity when using a MS/MS capable ICP-QQQ system operating using two tandem mass separations (one before and one after the collision reaction cell) – giving abundance sensitivity $<<1x10^{-10}$ with examples such as manganese in an iron-rich matrix and neptunium in a uranium matrix.

POSTER 1 - VENDORS I: 8

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation

Keywords: semi, semiconductor, sulfuric, phosphoric, preconcentration

Inline Preconcentration and Matrix Removal for Determination of Ultratrace Metals in Semiconductor-grade Phosphoric and Sulfuric Acid

Nathan Joe Saetveit, Daniel Wiederin

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Phosphoric and sulfuric acids are important reagents in semiconductor manufacturing processes, and semiconductor manufacturers are demanding increasingly lower levels of contamination for critical elements. Novel analytical techniques are required for the determination of some elements in these acids due to their high viscosity and the presence of matrix-based polyatomic interferences by ICPMS. The use of a reaction gas in ICPMS has been shown to improve the detection limits and successfully determine a variety of elements in these matrices, but some elements, such as Ti and Zn, are still difficult to determine at low-ppt concentrations with standard sample introduction.

This work describes a novel technique for automatic preconcentration and matrix removal of undiluted phosphoric and sulfuric acids for the attenuation of interferences and enhancement of detection limits for critical semiconductor elements. Undiluted acid is loaded onto a sample loop and automatically diluted and transferred to a secondary loop. During the transfer, a standard addition spike may be added, which allows automatic calibration by standard addition. After transfer, the unspiked or spiked sample is automatically loaded onto a preconcentration column for removal of the phosphate or sulfate matrix. Trace elemental impurities are then eluted directly to the ICPMS, resulting in low-ppt detection limits.

POSTER 1 - VENDORS I: 9

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation

Keywords: biological samples, sample preparation, calibration strategies

Multi element determination of various biological matrices using a unique calibration

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The better understanding of the relevance of various elements in metabolic and other processes in organisms leads to increased interest in the analysis of biological samples such as urine, serum, plasma and whole blood. Here, the focus is on supply of essential elements and detection of toxic elements. Fast and sensitive analytical techniques are necessary to satisfy these demands.

The transition from atomic absorption spectroscopy (AAS) s to inductively coupled plasma – mass spectrometry (ICP-MS) has been gradual over the past two decades for the clinical industry as the technique matures and demand grows. Both flame AAS and graphite furnace AAS, otherwise known as electrothermal vaporization AAS have served the clinical industry well in hospitals, clinical institutes, universities, health organizations and general industry for research, diagnostic and monitoring purposes. The strength of Atomic Absorption lies in its ability to accurately and precisely measure a large range of elements in various biological samples, including major, minor, essential and toxic elements from % levels down to parts per trillion (ppt), and even lower for some elements.

The ability to measure many elements over a short period time has seen ICP-MS become the instrument of choice in the clinical industry for elemental analysis. A large dynamic range and ultra-low detection limits superior to graphite furnace AAS means ICP-MS can meet the growing demands for more information in less time and with less complexity.

The method developed allows the determination of more than 20 elements in various biological matrices in the same sequence using a highly sensitive ICP-MS.

POSTER 1 - VENDORS I: 10

Poster presentation (vendor paper)

Topics: Elemental analysis, Environmental sciences, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Rare earth elements, geological, REE, ICP-MS, ICP-OES

Rare Earth Elemental Trace Analysis in Granite and Sandstone by High Resolution ARRAY ICP-OES and ICP-MS with iCRC technology

Rene Chemnitzer, Heike Gleisner, Rui Santos, Sebastian Wünscher, Jan Scholz, Andrew Jason Ryan
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Quantification of rare earth elements (REE) in geological and pre-processed materials by ICP techniques is one of the most challenging analytical routines. While trace detectability on conventional ICP-OES is often hampered by numerous spectral interferences (line overlap), in ICP-MS elaborate sets correction equations are typically used to deal with polyatomic rare earth oxide interferences.

Herein, we wish to report on significant improvements in precision, quantification limits and ease of use for REE analysis by (i) ARRAY ICP-OES with unique spectral resolution and (ii) ICP-MS with integrated collision and reaction cell (iCRC) technology. Comparative data collected for Granite and Sandstone CRM will be presented.

POSTER 1 - VENDORS I: 11

Poster presentation (vendor paper)

Topics: Environmental sciences

Keywords: clinical analysis, urine, serum, multiple cell gases, FAST

Simultaneous Multielement Determination in Urine and Serum Samples by Quadrupole Cell ICP-MS using FAST-Technique

Dr.Jörg Michel

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This poster is presenting a high productivity routine method for ICPMS allowing simultaneous analysis of 25 analytes in urine and 28 in serum samples. The use of a SC-FAST sample introduction system allows automatic addition of internal standard to each sample, short analysis time and high sample throughput. The applied sample preparation is using commercial matrix matched lyophylised calibrators and a simple one step dilution into a slightly acid diluent. Instrument calibration was carried out by a three level calibration utilizing these calibrators. By combining advanced sample introduction with state of the art interference reduction from a quadrupole cell operating in collision and reaction mode, accurate multielement determinations in demanding urine and serum matrices are straightforward. Method performance is demonstrated by stability and recovery experiments of approved clinical control materials which showed good agreement with certified values.

POSTER 1 - VENDORS I: 12

Poster presentation (vendor paper)

Topics: Application of speciation analysis

Keywords: USP 232, speciation, arsenic

Speciation of Arsenic in Drugs and Excipients for compliance with USP <232> and ICH Q3D

Jonathan Sims, Helmut Ernstberger

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Complying with testing requirements for Arsenic as specified in both USP <232> and ICH Q3D can require speciation in order to risk assess cases where the total measured Arsenic exceeds the permitted daily exposure (PDE). The stated PDE's apply to drug products, but also excipients and drug substances used in the manufacture of the product may need to be monitored for metal impurities to demonstrate appropriate control of the quality of the finished product.

We report arsenic results for some common drug substances and excipients used in over the counter medicines using LC-ICP-MS on a NexION 350 instrument. The results were validated using spike recoveries for inorganic arsenic species, demonstrating the suitability of the presented method for pharmaceutical analysis.

POSTER 1 - VENDORS I: 13

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation, Isotope ratio analysis

Keywords: ICP-MS, multi-collector, desolvation, nebulizer, sample introduction, isotope ratio

Using a Desolvating Nebulizer System with Inductively Coupled Plasma Mass Spectromtery: Key Optimization Parameters

Bill Spence, Fred Smith, Peter Winship

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Multicollector ICP-MS instruments are very specialized devices for high precision isotope ratio measurements. For useful measurement of low abundant isotopes and mass-limited samples, signal enhancement is often required. In addition, sample preparation and/or sample aerosol desolvation may be necessary to reduce or eliminate mass spectral interferences such as oxides and hydrides.

This poster will examine key optimization parameters of a desolvating nebulizer system for high and stable analyte signals with lowest backgrounds. Experimental parameters such as nebulizer gas flow, argon sweep gas flow (outside the membrane desolvator), nitrogen addition gas (post membrane), and ICP-MS ion optic voltage settings will be examined. In addition, setup of the sweep gas outlet line and trap bottle will be discussed in relation to minimization of localized condensate buildup.

POSTER 1 - VENDORS I: 14

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation
Keywords: MP-AES, HF, inert sample introduction system, Nickel alloy

Direct determination of Al, B, Co, Cr, Mo, Ti, V and Zr in HF acid-digested nickel alloy using the Agilent 4210 Microwave Plasma-Atomic Emission Spectrometer

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Nickel alloys are used when good high- and low-temperature strength and corrosion resistance are needed. Typical industrial applications are for fabrication of chemical and petrochemical process vessels and gas turbine parts. The aerospace and military industries are also important users of nickel based alloys, which are frequently used in the manufacture of jet engine parts including turbine blades. The additive elements in the nickel alloy and their concentrations are carefully selected in order to obtain the desired material properties. For example, titanium (Ti) is added to improve corrosion resistance and increase the strength-to-density ratio of the alloy.

It is also known that low concentrations of boron (B) and zirconium (Zr) improve material hardness. A slight change in composition can adversely affect the properties of the alloy. Therefore, accurate elemental analysis of nickel alloys is extremely important from the metallurgical and engineering point of view. The certified reference material (CRM) IN 100 alloy–cast, which is a nickel based alloy that provides high rupture strength at high temperatures was used for elemental analysis. Hydrofluoric (HF) acid must be employed during sample preparation to ensure complete dissolution of alloys containing elements such as Ti, Zr, Hf, Nb, Ta, Mo, W, Ge, Sn or Sb. Therefore, for this application the inert torch for the 4200/4210 series MP-AES was used in conjunction with an inert double-pass spray chamber and the inert OneNeb Series 2 nebulizer, to facilitate the direct analysis of HF digests without prior neutralization.

The results from analysis of the IN 100 nickel alloy CRM were within 10 % of the certified values, this demonstrate that the Agilent 4210 MP-AES is an excellent technique for the analysis of challenging metallurgical samples. The wide dynamic range capability was demonstrated as elements were determined over a wide concentration range from hundreds of ppm to % level in the same sample, without any pre-analysis dilution, in a single reading with excellent recoveries. Good long term stability was also demonstrated for continuous measurement of the IN 100 nickel alloy CRM over a period of 8 hours with precision of less than 5% RSD. FLIC (Fast Linear Interference Correction) was able to successfully model the complex interferent signals and apply correction, ensuring good results for all elements with excellent recoveries across a concentration range of three orders of magnitude.

POSTER 1 - VENDORS I: 15

Topics: Sample introduction and sample preparation

Keywords: Clinical Samples, ICP-MS, Urine, Serum, Selenium

Easy & fast determination of trace elements in clinical samples using quadrupole ICP-MS

Jan Knoop[1], Nils Garnebode[2], Konstantin Kartaschew[2], Uwe Oppermann[1], Ludivine Fromentoux[3]

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For the determination of trace elements in urine and serum, different measures must be considered to achieve correct results. While it is quite easy to determine trace elements in urine after dilution (x10), the same is getting more challenging for serum matrix, due to the higher amount of carbon and subsequent appearing interferences for example for the determination of selenium.

In general ^{78}Se is most common isotope to be selected for quantification of selenium. Typical polyatomic interferences of $^{38}Ar^{40}Ar$ can be solved using kinetic energy discrimination (KED) mode by an efficient octopole collision cell (helium). But with increasing carbon matrix samples, the influence of Ar polyatomic interferences are present in different levels, as the argon now forms carbides in addition.[1] That is why e.g. working with reaction cells could be an alternative way to achieve correct Se-levels within the samples, but this requires additional measurement modes and is more time consuming if other elements are of interest at the same time.

To develop a fast method for multi-element determination in serum, matrix matching of calibration solutions overcomes the negative influence of carbon matrix samples (like serum) and makes it possible to determine different elements within a short time without using additional reaction gases.

This poster shows how to matrix match the calibration solutions to find an easy way to determine trace elements in different clinical samples and how to find out which concentration of carbon is required to be present within the calibration solutions, using the ICPMS-2030 (Shimadzu) with and without kinetic energy discrimination mode.

[1]Nelms, Simon M., Inductively Coupled Plasma Mass Spectrometry Handbook, CRC Press LLC, 2005

POSTER 1 - VENDORS I: 16

Topics: Elemental analysis

Keywords: Wine analysis, heavy metals, ICP-MS, polyatomic interferences

Determination of heavy metals in Italian wine using ICP-MS

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For simultaneous quantitative determination of the inorganic elements in wine, ICP-MS is the most preferable tool for quality control because of a high sensitivity (trace detection), a wide dynamic range and a high sample throughput. The Shimadzu ICPMS-2030 constitutes an easy and fast system to meet this requirement. Due to the unique Eco-mode system associated with Mini-torch, ICPMS-2030 is able to drastically reduce running cost.

Even though, wine is regarded as a difficult matrix because of the high number of constituents, the octopole collision cell assures a high accuracy for all element measurement. Using Helium gas and Kinetic Energy Discrimination principle, this cell suppressed most of the spectroscopic interferences (polyatomic interferences). Efficiency of interferences suppression and sensitivity are improved by a cooled cyclonic chamber and well controlled torch positioning.

In this study some commercially available red and white wines from Italy are used : three white wines Gavi, Critone, Lugana and three red wines Montalcino, Chianti, Magliano.

Thanks to the ICPMS 2030 system, analysis of wine could be performed with a minimum effort on sample preparation. All samples analyzed here are only diluted 1:3 with 1 % Nitric acid to decrease the ethanol levels around 4%. After this treatment they are directly aspirated for analysis by ICPMS-2030. 14 different elements are simultaneously quantified : As, Cd, Cs, Cu, Cr, V, Fe, Mn, Ni, Pb, Se, Sn, Tl and Zn. Analytical measurement conditions have been optimized and data sets of the wine samples will be presented.

POSTER 2 - APP II: POSTER SESSION 2: Applications II

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com SOUTH HALL

POSTER 2 - APP II: 1

Topics: Archaeometry and forensics

Keywords: LA-ICP-MS, conflict minerals, proof of provenance, statistics

Checking the supposed provenance of conflict minerals based on LA-ICP-MS data and statistics

Hans-Eike Gäbler, Wilhelm Schink, Timo Gawronski

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Ongoing violent conflicts in Central Africa are fueled by illegal mining and trading of tantalum, tin, and tungsten ores (TTT ores). Traceability systems aim to foster market access for ore minerals which are not conflict-affected and meet ethical standards for mineral exploitation. The credibility of document based traceability systems can be improved by the analysis of mineral samples to obtain the so-called 'Analytical Fingerprint (AFP)'. AFP shall be applied as an independent tool to confirm or doubt the documented origin of the TTT ore minerals coltan, cassiterite, and wolframite.

TTT minerals are mined from pegmatites or quartz veins which are small geological units with dimensions in the range of tens up to several hundreds of meters. Minerals originating from the same pegmatite or quartz vein are subject to the same geological processes and should therefore reveal similar geochemical compositions. However, differences in the composition of the fluid from which the mineral grains crystallize lead to substantial variability in the trace element compositions of individual mineral grains mined from the same ore body. The similarity of the geochemical composition of mineral grains from a common source on the one hand and the high variability between them on the other hand as well as the fact that ore concentrate samples are not representative aliquots of their ore body have to be taken into account in the development of an AFP method.

A continuously increasing database of reference samples from many different mine sites (actually about 250) in Central Africa has been set up to perform AFP. A sample in question can be compared to the reference sample from the supposed origin. The challenge which has to be met is to assess the degree of similarity between these two samples.

Typical sample properties in terms of main and trace element concentrations can be obtained by LA-ICP-MS. Ore minerals are traded as so-called ore pre-concentrates which are the result of simple ore processing steps (e.g. crushing, panning, and concentration of the valuable ore minerals) on or nearby the mining site. From an ore concentrate only ore mineral grains are analyzed. Polished sections containing hundreds and up to several thousands of mineral grains are prepared from each ore concentrate. The respective ore minerals are identified by using scanning electron microscopy combined with automated mineralogy. After the identification step about 50 grains per ore mineral are analyzed by LA-ICP-MS for about 30 - 50 elements. The resulting distributions of element concentrations from ore concentrates can be used to assess the similarity between two ore concentrate samples.

Based on the Kolmogorov-Smirnov distance, a measure of similarity between a sample in question and reference samples from a database is determined. Decision criteria are deduced empirically to identify samples which do not originate from the declared mine site.

POSTER 2 - APP II: 2

Topics: Elemental analysis

Keywords: Bromine, Iodine, ICPMS, Polymers

Determination of Br and I in polymers by ICPMS

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Organobromine compounds have been widely used as flame retardants due to their inhibitory effect on combustion chemistry and to their reduction of the flammability on products containing them. The impact of brominated flame retardants (BFRs) on the environment and their potential risk in animal and human health is a present concern. Therefore, existing legislation in the European Union, specifically, the Restriction of Hazardous Substances (RoHS) Directive (2002/95/EC) limits the use of certain products in electrical and electronic equipment released to the market since 1 July 2006.

Iodine and its compounds are very active catalysts in the production of synthetic rubber or stereospecific polymers, such as polybutadiene rubber and polysoprene polymers. Iodine also is added to certain polymers to change the color, the morphology, the complexation sites or regions, the biological activity, and the electrical conductivity. In addition iodine polymeric complex has antimicrobial, antifungal, anti-inflammatory and astringent properties.

In this work, a method for Br and I determination in polymers is proposed. No memory effects were observed on iodine or bromine determination under alkaline conditions. Good recovery factors and detection limits were obtained for both elements.

POSTER 2 - APP II: 3

Topics: Elemental analysis

Keywords: ICP-MS, wine, geographical authenticity

ELEMENTAL DIFFERENCES IN SINGLE VINEYARD PINOT NOIR WINES FROM SIX SUB-APPELLATIONS

Helene Hopfer[1], Courtney Tanabe[2], Joshua Godshaw[2], Susan Ebeler[2], Jenny Nelson[2], Roger Boulton[2]

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The geographical authenticity of food products is of high interest for consumers, especially for products where geographical origin is associated with certain qualities. Previous studies have looked at this at a rather large geographical scale, i.e., across countries or across winemaking regions within one country. For this study, we attempt to discriminate wines from six sub-appellations within one winemaking area, with three or five different vineyards in each sub-appellation. Mono-varietal Pinot noirs were collected as single vineyard lot wines from 28 neighboring vineyard sites within one American Viticultural Area (AVA) in Northern California, USA. All wines were made at each winery with minimal oak contact and without significant additions other than yeast and nutrient additions during winemaking.

For analysis with Inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 8800) wines were diluted 1:3 in 5% Nitric Acid (v/v) prior to analysis. An IS mix (Agilent), covering the m/z range from 6 to 238 was mixed with the sample stream in a mixing tee before entering the micromist nebulizer. Elements were monitored in helium, high energy helium or oxygen mode in the ORS3 collision/reaction cell. Matrix-matched (4% ethanol, 5% HNO_3) 6-point calibration curves for each element were established between 0.1 and 500 µg/L using multi-element standards (Agilent). For the higher concentrated elements (B, Na, Mg, Si, P, S, K, Ca, Mn, Fe, Rb, Sr), microwave plasma-atomic emission spectroscopy (4200 MP-AES; Agilent) was used, because the MP-AES instrument was available. Samples, diluted 1:3 in 5% HNO_3, were mixed with 2,000 mg/L ionization buffer solution prior to entering the system. Matrix-matched calibration curves (4% ethanol, 5% HNO_3) were established for each individual element based on original ICP-MS data. Analysis of variance was used to determine statistical significant differences across the sub-appellations. Further, discriminant analysis was carried out using linear and non-linear transformations of elemental concentrations. Single elements as well as ion uptake ratios and ion groups were used to study potential impacts of water sources.

Recovery for all detected elements was within ± 20% of the target concentration. Sixty elements were detected in the 28 wines above their detection limits, and significant differences in the concentration of 43 elements across the six sub-appellations were found. Origin of the elements that differed across the six sub-appellations could be explained by both endo-and exogenous processes (vineyard soil, viticultural practices, irrigation, processing, winery equipment).

POSTER 2 - APP II: 4

Topics: Elemental analysis

Keywords: ICP-OES, whiskey, elemental fingerprints

Elemental profiles of whiskies allow differentiation by type and region by inductively coupled plasma – optical emission spectroscopy (ICP-OES)

Jenny Nelson[1,2], Helene Hopfer[4], Greg Gilleland[3], Susan Ebeler[1,2]

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Elemental fingerprints could provide an analytical approach to product differentiation and authentication, and have been used in the past for various distilled spirits, including brandy, gin, bourbon and tequila. However, a comparison of elemental differences between different whiskey types, such as Bourbon and Scotch, was still missing. In this study we compare the elemental fingerprints of 68 commercial whiskies for differentiation due to type (Bourbon, Tennessee, Scotch, Irish, Japanese) and region. Concentrations from sub-mg/L to mid-mg/L of 53 different elements were determined with inductively-coupled plasma – optical emission spectroscopy (ICP-OES) and used in subsequent statistical analyses by Mass Profiler Professional (MPP). Significant differences in several elements were found for type, and allowed a classification according to whiskey type. Elemental differences were also found for different production areas within Scotland, thus, providing further evidence that Scotch whiskies could be differentiated by elemental analysis. Major sources of elemental differences seem to be processing equipment and raw materials, such as water.

POSTER 2 - BI: POSTER SESSION 2: Bioimaging

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com NORTH HALL

POSTER 2 - BI: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: exposure, mercury, hair, teeth, blood

Characterizing human contaminant exposure and elimination by laser ablation ICP-MS

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Archived blood spots, hair and teeth may provide a valuable measure of past trace element exposure. Under controlled experimental conditions, hair in particular can be used to provide a minimally invasive record of trace element exposure changes over time in a single sample that otherwise would require serial blood samples over time. We have used LA-ICP-MS, specifically a NWR 213 LA unit coupled to an Agilent 8800 ICP-MS, in studies of teeth, hair and blood to investigate trace element exposure and elimination. We have investigated the use of external blood spot standards for quantitative LA-ICP-MS analysis of historic archived blood spots. Comparison of conventional (digestion and solution analysis) ICP-MS data with the LA-ICP-MS data showed good correlation for most elements and quantitative agreement when Fe was used as an internal standard for the LA-ICP-MS approach; which indicates the importance of normalizing the desiccation/dryness state of the blood spot standards and samples. We also have used spatial analysis of single hair strands for Hg (normalized to S) to provide a temporal record of an individual's dose and elimination of Hg in a controlled feeding study. Calculated elimination rates are in general agreement with the few existing studies but also reveal wide individual variability which is the focus of future studies. Spatial analysis of teeth has been used to provide a temporal record of exposure to elements such as Pb, Mn. In addition to these elements we are assessing the feasibility of teeth analysis for Cd, Hg and As. Our preliminary studies have involved analysis of NIST bone meal standards spiked at the low ng/g concentration range for these elements. We have investigated the high sensitivity and flexibility of using varied reaction gases of the 8800 QQQ ICP-MS to establish detection limits for these elements in a hydroxyapatite matrix.

POSTER 2 - BI: 2

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Nanomaterials
Keywords: imaging, cells, nanoparticles

High resolution laser ablation NWRimage system for single cell imaging

Diego Esteban-Fernandez[2], Heike Traub[3], Norbert Jakubowski[3], Katherine McLachlin[1], Leif Summerfield[1], Rob Hutchinson[1]

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The traceability and availability of nanoparticles enables their use to enhance a variety of nano-biological and nano-medicinal applications. The particular size and shape of nanoparticles determine the uptake rate and pathway into the cell, and therefore impact specific cell components and processes. Selecting specific particle types allows researchers to target the process or structure of interest, with minimal additional impact. This can be used for drug or DNA delivery, and is being explored for use in oncology. Understanding the different uptake mechanisms and impacted processes requires sub-cellular imaging resolution to determine, for example, whether or not the nanoparticles are reaching the nucleus.

Sub-cellular imaging has traditionally been challenging to achieve with laser ablation ICP-MS due to a lack of sensitivity at small spots. Bioimaging using LA-ICP-MS is a well-established technique, but usually applied on the tissue scale, which depends on larger spot areas where sensitivity is less problematic. The improved sensitivity and washout from the NWRimage has allowed faster imaging of smaller spots. The NWRimage also provides the possibility of true sub-micron spot sizes. This work compares the capabilities of standard laser ablation (NWR213 system) with results from the NWRimage platform, which has been optimized for imaging applications.

POSTER 2 - BI: 3

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics
Keywords: LA-ICP-MS, Selenium, Collision Cell, Reaction Cell, bio-imaging

The impact of reaction and collision cell ICP-MS on laser ablation bio-imaging

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Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) has become a popular tool for bio-imaging applications. Most elements can be detected under normal ICP-MS conditions, but for elements such as selenium (Se) the addition of a reaction or collision cell is needed for accurate measurements. For LA-ICP-MS imaging all data needs to be collected simultaneously. This means that any additional elements scanned for in combination with Se would need to also be analyzed under collision or reaction cell conditions. This report will compare kidney samples analyzed using LA-ICP-MS under normal, reaction cell, and collision cell ICP-MS parameters. These effects will be demonstrated using the elemental responses of Se, P, S, C, Cu, and Zn.

POSTER 2 - BI: 4

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Coupling techniques (chromatography, FFF, ETV, others)

Keywords: Aged-Related Macular Degeneration (AMD), Drusen formation, Quantitative speciacion, Imaging, Laser ablation ICP-MS

Development of new strategies based on HPLC- and LA-ICP-MS to study the Zinc-Metallothionein system in the human eye and its implication in Age Related Macular Degeneration

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Aged-Related Macular Degeneration (AMD) is the leading cause of irreversible blindness among people older than 60. The hallmark of AMD is the build-up of extracellular deposits (drusen) between the retinal pigment epithelium (RPE) and Bruch's membrane. These deposits can reach millimolar levels of Zn. Metallothioneins (MTs) are the main cytosolic zinc-binding proteins, involved in neuroprotection and defense mechanisms against oxidative damage. We previously proposed the system Zn-MT as a potential therapeutic target of AMD. Molecular biology and optical microscopy-based methodologies are not enough to study the role of Zn and MTs in drusen formation and, therefore, the use of complementary tools based on Mass Spectrometry may contribute to the understanding of this disease. In this sense, the development of new methodologies for Zn-MTs quantification and localisation in eye tissues may provide valuable information about the molecular processes occurring in AMD.

- **Methods**

Advanced methodologies based on High-Performance Liquid Chromatography (HPLC) and Laser Ablation (LA) coupled to ICP-MS will be presented for the comprehensive study of Zn-MTs role in ocular tissues and cells. We have developed a quantitative speciation methodology using HPLC-ICP-MS with post-column isotopic dilution analysis (IDA) to study the Zn-MTs redox system in ocular tissues (RPE and Retina) and in an *in vitro* model of RPE cells. Furthermore, calibration using gelatine standards was performed to obtain quantitative images of Zn distribution into ocular tissue sections by LA-ICP-MS.

- **Results**

The study of Zn-MTs levels in the RPE *in vitro* model under exposure to different drugs inducing the synthesis of MTs was successfully investigated. Experimental results obtained at protein level by IDA-HPLC-ICP-MS were found to be in agreement with results obtained at RNA expression level. In both cases, isotopically enriched Zn was the best Zn-MTs inductor. In addition, we carried out a quantitative speciation study of Zn-binding proteins, in RPE and Retina tissues from post mortem donors.

A bio-imaging quantitative methodology has been also developed to study the distribution of Zn directly in human ocular tissues. Quantitative images of Zn in cryogenic sections analysed by LA-ICP-MS are presented. A higher accumulation of Zn was observed in the area of RPE compared to that observed in retina and sclera regions. Furthermore, experimental results obtained by LA-ICP-MS were validated by the analysis of digested tissues using conventional nebulization ICP-MS and compared with microscopy images obtained by using a Zn ion probe.

- **Conclusions**

Two complementary methodologies for comprehensive study of Zn-MTs role in ocular tissues and cells by HPLC- and LA-ICP-MS have been successfully developed. Thus, further experiments will be performed with tissues from AMD patients that could help us to understand, for example, the importance of Zn and MTs in drusen formation.

POSTER 2 - BI: 5

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Dental implants, LA-ICP-MS, Soft tissues, Calibration strategies, Bioimaging

Mapping Ti, Al and V originated from dental implants in oral mucosa tissue by LA-ICP-MS

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In order to measure content of elements in sample it is the most often previously converted to liquid form via mineralization step. As an effect, one obtains only averaged content value with no information of spatial distribution of elements on the sample surface. The method of LA-ICP-MS is capable to measure elements in solid sample and produce data in form of 2D maps of content with spatial resolution as low as 10 μm.

LA-ICP-MS was used in the study of soft tissues which were in direct contact with metallic parts of dental implants: intraosseous part and closing screw. The materials used for the manufacture of implants and cover screw were grade 4 pure titanium and Ti6Al4V alloy containing 90% Ti, 6% Al and 4% V. The samples were collected from patients treated with dental implants. Fragment of oral mucosa before implantation served as a control group sample.

Measurements were made using a quadrupole ICP-MS (Elan DRC II, PerkinElmer) with a laser ablation system (LSX-500, Cetac). In order to obtain quantitative data a calibration approach based on matrix matched solid standards with analyte addition was developed and applied. Dynamic ablation of sample surface was carried out, line by line with laser beam diameter of 100 μm, which allowed us to present data as 2D maps. Results show that oral mucosa samples have much higher analyte content in comparison to control group samples. Signals are usually located in small regions with sharp edges, however, also larger and more scattered areas with elevated content are visible. This is due to the forms in which analytes occur in soft tissues: as ions and as metallic particles. During the insertion of implant and as an effect of material wear and electrochemical dissolution metals can migrate from implants to the surrounding tissues in form of ions and particles with diameter of nm and μm.

This work was financially supported by the Research Project of the National Science Centre Poland (2015/17/N/ST4/03808).

Literature:

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POSTER 2 - BI: 6

Topics: Metallomics, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Laser Ablation, ICP Triple Quadrupole, Cellular Resolution, NSF, Prostate Cancer

LA-ICP-QQQMS for the High Resolution Elemental Bio-Imaging of Trace Elements

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The potential to investigate diseases associated with trace elements has attracted significant interest in the past decade. Trace elements incorporated in proteins or interfering with endogenous structures are thought to play key roles in many diseases. However, respective concentrations are sometimes below the detection limits of currently applied methods. Furthermore, a decrease in the lateral resolution always requires a sacrifice of sensitivity. Therefore, in order to obtain cellular resolution of trace elements, an improvement in the detection limits is necessary.

In this work, a novel technique employing laser ablation coupled to an inductively coupled plasma mass spectrometry system equipped with a triple quadrupole (LA-ICP-QQQMS) is presented. Two different methods were developed in order to push the detection limits and to allow the imaging and calibration of target elements, which usually cannot be calibrated with a respective single quadrupole system (ICP-QMS). Analysis was conducted either with a new MS/MS approach or with a bandpass mode. The quantitation of element was achieved by means of an external calibration with matrix matched standards. Finally, the results were compared with a LA-ICP-QMS in order to reveal improvements and advantages. The new methods were used to investigate the gadolinium (Gd) distribution on cellular resolutions in samples from a patient suffering from nephrogenic systemic fibrosis (NSF). Additionally, the correlation of Gd with different elements was studied in order to study the molecular mechanisms triggering NSF. Second, elements which are believed to be bio indicators for prostate cancer were investigated in order to supply new methods in the diagnosis and classification of cancer.

For the investigation of Gd in NSF samples, an improvement associated with the additional quadrupoles decreased the detection limits significantly and allowed the imaging with high spatial resolution at cellular levels. Correlation studies of Gd with different elements such as zinc, phosphorus and calcium allows a suggestion of the molecular mechanism triggering NSF.

The operation of the LA-ICP-QQQMS system in the bandpass mode allowed the quantitative bio-imaging of trace elements, such as manganese (Mn), copper (Cu), iron (Fe) and zinc (Zn). These elements are incorporated in metalloproteins which are overexpressed in prostate tumours. Thus, imaging of these elements enabled the visualization of the altered metabolism. Here, the first quadrupole works as a pre-filter increasing the ion transmission. Drawbacks in terms of increased backgrounds and interferences could be compensated with the remaining quadrupoles.

POSTER 2 - BI: 7

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Archaeometry and forensics
Keywords: arsenic, diagenesis, bio-imaging, teeth, LA-ICP-MS

Investigating Biogenic versus Diagenetic Arsenic Incorporation in Sheep's Teeth

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Since elevated arsenic concentrations were found in modern day smelter worker's bones and teeth, arsenic concentrations in archaeological skeletal remains, and even in hair, have been taken into consideration as indicators for past smelter-working. However, it has become evident that under certain burial conditions diagenetic alteration (chemical, physical and biological degradation of material after deposition) causes increased arsenic concentrations in these tissues. Further understanding of how arsenic accumulates, both *in vivo* and diagenetically, is thus required to enable the interpretation of arsenic levels in skeletal remains.

In this study, the accumulation of arsenic in teeth of modern-day sheep is investigated. Teeth were obtained from (1) seaweed-eating sheep from the Orcadian island of North Ronaldsay, naturally exposed to high amounts of arsenic (about 35 mg As per day, of which about 86 % bioavailable), (2) grass-eating sheep from the Orcadian island of Hoy on a low-As diet, and (3) grass-eating sheep from Bettyhill, on the north coast of the Scottish mainland, on a low-As diet.

Total As concentrations in pooled dentine, cementum and pulp samples using HG-AFS revealed As concentrations ranging from 0.3 ± 0.03 to 2.9 ± 0.2 mg/kg in seaweed-eating sheep, over two orders of magnitude higher than in similar samples from grass-eating sheep. While concentrations vary significantly between individual sheep, it was found that variation in As concentration in second and third molars from the same individual was much lower.

Semi-quantitative bio-imaging of sheep's teeth cross-sections by LA-ICP-MS showed As accumulation to be highest in tooth cementum, and to a lesser extent in occlusal dentine (exposed dentine on the chewing surface). This pattern was visible in molars from sheep exposed to high levels of dietary As, as well as in teeth from sheep exposed to lower levels of As. Metabolic processes may have led to incorporation of As into the cementum, however due to the patterning of As on the occlusal surface, it suggested here that the accumulation of As occurred during mastication, indicating processes similar to those of diagenetic alteration occurring *in vivo*.

POSTER 2 - BI: 8

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics, Nanomaterials
Keywords: Gold nanoclusters, Imaging, LA-ICP-MS, Metallothionein, Immunoassay, ocular tissues

Bioimaging of Metallothioneins in ocular tissue sections by LA-ICP-MS using bioconjugated gold nanoclusters

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Oxidative stress is produced by an imbalance between free radical production and biological system's ability to detoxify the reactive intermediates and repair the resulting damage. In the human eye the main causes of oxidative stress are the daily exposure to sunlight, chemical insults and the special microenvironment with abundant photo-sensitizers. For this reason, oxidative stress has been associated several ocular diseases, like aged-related macular degeneration (AMD).On the other hand, Metallothioneins (MTs) are a family of low molecular weight (6–7 kDa), cysteine-rich (30%) and metal-binding proteins. The cysteine residues can bind metal atoms such as zinc, copper, and cadmium via thiolate bonds. These proteins have a wide range of functions including defense against oxidative damage, intracellular storage and transport and metabolism of metal ions. The antioxidant properties of MTs reside in their capacity to capture and neutralize free radicals by binding and transferring zinc ions in a redox-dependent fashion, forming the antioxidant system Zinc-Metalothionein (Zn-MT)[1].

Highly sensitive analytical tools are required to study the relationship between Zn and MTs in sections from ocular tissues. These methodologies should permit the simultaneous localization (bioimaging) of metals and proteins. Laser ablation (LA) coupled to ICP-MS has shown a huge potential for bioimaging studies in biological tissues. In addition, the use of metal nanoclusters (NCs) as elemental tags will provide signal amplification, compared with other tags traditionally employed (e.g. polymeric tags). To this end, antibodies with gold nanoclusters (AuNCs) will be used in combination with LA-ICP-MS for the detection of different metallothioneins (MT 1/2 and 3) directly into the ocular tissue sections.

- **Methods**

The AuNCs synthesized were bioconjugated with an Anti-MT 1/2 antibody and with Anti-MT 3 antibody. Next, using ocular tissue sections (5 microns thick) from different donors the immunoassays were performed. After the immunoassay protocol, imaging studies were carried out by LA-ICP-MS as well as by fluorescence (confocal microscope) in order to compare both methodologies.

- **Results**

The MTs (measuring the Au signal) and the coordinated metals distribution (Zn and Cu) were successfully carried out in human ocular tissues, including sclera, choroid, retina and retinal pigment epithelium regions. The image patterns found in ocular tissues were in agreement with those reported by conventional immunohistochemistry.

- **Conclusions**

It is possible to know the distribution of MT proteins and different coordinated metals using bioconjugated AuNCs and LA-ICP-MS. Proposed analytical tools could help to better understand the roles of the antioxidant system Zinc-Metalothionein in the eye.

- **References**

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POSTER 2 - ENV: POSTER SESSION 2: Environmental analysis

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com NORTH HALL

POSTER 2 - ENV: 1

Topics: Elemental analysis, Environmental sciences

Keywords: monitoring, aluminium, field study, accredited method, drinking water

Monitoring of aluminium, used as a coagulant in a potable water treatment plant, field study.

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Water-link is the total water solutions supplier of Antwerp and 7 municipalities. The company has evolved into the largest drinking water producer in Belgium, not only delivering drinking water to residential customers but also to other drinking water companies and the manufacturing industry. During the purification of surface water to drinking water, aluminium is added as a coagulant under the form of polyaluminium chloride (PAC). After flocculation or decantation followed by filtration, the formed flocks are removed from the water. The dose of PAC is based on the monitoring temperature and pH. To control the actual removal of the flocks, the concentration of aluminium in the water is determined. During the purification process samples of the effluent of the different sand filtration plants are collected. The aluminium profile is monitored throughout the complete distribution network (conform EC regulation 98/83/EU). A fully validated and ISO 17025 accredited method was optimized for the monitoring of aluminium using ICPMS. Results of optimization, validation and a field study will be presented.

POSTER 2 - ENV: 2

Topics: Environmental sciences

Keywords: Uranium, Alfa activity, Drinking water, ICP-MS

ICP-MS, a useful technique for the determination of uranium and estimation of alfa activity in natural and drinking water

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International regulations and recommendations for drinking waters have traditionally included maximum radioactivity levels due to the harmful effects on health of some radionuclides which can be present in natural waters, both of natural or antropogenic origin. The European Directives 98/83 EC *on the quality of water intended for human consumption* and 2013/51/EURATOM *laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption*, do not regulate the uranium concentration directly, but establish a maximum level for alfa activity (0.1 Bq/L). In case this value is reached, uranium isotopes (U-238, U-235, U-234) and other alfa-emitters have to be analysed and the potability level is established taking into account a maximum value for the indicative dose, 0.1 mSv/year. The individual radionuclides are analysed by radiometric techniques and results are expressed in activity units.

According to a WHO-EC project to review the list of parameters to be considered in the European regulations, uranium will probably be included in the next future, following the steps of USEPA and WHO Guidelines. Both chemical and radiological considerations would be taken into consideration when reference levels are set, and the parameter would be regulated in concentration units (parametric value: 30 µg/L) instead of activity ones.

ICP-MS has shown to be a useful technique for the analysis of uranium in different types of samples. The present work has two objectives: first, to demonstrate that the quality parameters of the technique are adequate for the water supply field (limit of detection, accuracy and precision); and second, a study of the possible correlation between the alfa activity by radiological methods and the uranium by ICP-MS in natural waters.

POSTER 2 - ENV: 3

Topics: Elemental analysis, Environmental sciences

Keywords: Humic substances, iron, SEC, estuarine mixing zone

Humic substance derived ligands as iron chelators in the ocean

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Iron is an essential micronutrient for many marine organisms, but concentrations in the open ocean are very low (below 1 nM in surface waters) and therefore it is a growth limiting factor. The iron in the dissolved organic matter fraction is almost entirely bound to organic ligands of poorly understood structure. It is assumed that marine bacterial siderophores belong to the most important iron carriers. The input from rivers has been considered as less important due to estuarine sedimentation processes of the mainly colloidal iron particles. However, recent studies have shown that this removal is not complete and riverine input may represent an important iron source in the open ocean. In this context, iron transport by peat-bog-derived humic substances (HS) has been identified as an essential carrier mechanism for riverine iron. The aim of our work is to characterize iron-complexing compounds in waters with varying concentrations of seawater simulating estuarine conditions in order to help understand which role peat-bog derived iron-HS compounds play in the open ocean. Suwannee River natural organic matter obtained from the International Humic Substance Society and water samples from the Craggy Burn River in Scotland were investigated. The experimental strategy employed offline pre-fractionation by size exclusion chromatography (SEC). Furthermore, selected SEC fractions were analyzed by non-targeted LC-TOFMS. First results will be presented and discussed.

POSTER 2 - ENV: 4

Topics: Elemental analysis, Environmental sciences
Keywords: phosphorus, ICP-OES, oceans, dissolved solids

Determination of phosphorus in high dissolved solids solutions to assess nutrient behaviour in ancient oceans

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A method for analysing the phosphorus in very high dissolved solids (185 mg L^{-1}) solutions has been developed. The high dissolved solids cause major problems with the analysis. The method developed allows us to analyse these samples and enables us to gain a much deeper insight into the history of our planets oceans that would not have been possible before this.

For the majority of Earth's history, the ocean has been in a state where no dissolved oxygen is present. Despite this the cycling of nutrients under these conditions is poorly understood. Phosphorous is a major nutrient and therefore it is essential to constrain its behaviour under these conditions to further our understanding of ancient ocean conditions.

We took samples from Lake La Cruz in Spain which has steep sides and strong chemical stratification with permanently anoxic bottom waters. These oxygen free and iron-rich waters are an ideal system to assess the nature of iron and phosphorus cycling on the ancient oceans.

We investigated the partition of iron and phosphorus between key phases using a phosphorus sequential extraction technique. This will ultimately improve our understanding of the associated feedback mechanisms that controlled the chemical nature of the biosphere during these periods of Earth history.

One of these extractions contains total dissolved solids (TDS) of 185 g L^{-1} and is therefore a significant analytical challenge. Phosphorus concentrations were expected to be relatively low in this extraction and a detection limit of 0.1 mg L^{-1} was required.

A method of analysis was developed using a Thermo iCAP 7400 radial ICP-OES to determine phosphorus in this matrix. A Miramist nebuliser was used in conjunction with an argon humidifier. Cobalt was used as an internal standard after yttrium was found to be unstable in the matrix. The instrument was optimised to provide highest possible signal to background ratio.

The method was shown to be stable over four hours by repeated measurements of the same sample for 4 hours. Appropriate rinsing of the sample introduction between samples was found to be critical in maintaining instrument stability and overcome high salting of the torch and injector.

The accuracy of the method was assessed by spiking samples with phosphorus and recoveries of 98-100 % achieved. The uncertainty associated with the method was assessed by repeated measurement of a sample over a period of 6 days and found to be 1.5 % using a 95 % confidence interval.

The detection (DL) and quantification limits (QL) were assessed by repeated measurement of the blank matrix over a period of 6 days. The high TDS of the matrix significantly supressed the phosphorus signal and phosphorus contamination within the matrix reagents used mitigated against achieving low DL however a DL of 0.10 mg L^{-1} and a QL 0.35 mg L^{-1} was achieved.

The method was used to analyse all samples from Lake La Cruz and is now in routine use for further research projects.

POSTER 2 - ENV: 5

Topics: Environmental sciences
Keywords: Long lived radionuclides, isotopic ratios, HR SF ICP-MS, method validation

Applications of Isotopic Measurements for Determination of Long Lived Radionuclides in the Open Ocean

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The survey of the marine environment is of primary importance in order to protect the health of marine ecosystems.

Nuclear and isotopic techniques are currently providing an unique source of information for identifying long lived radionuclides and tracing their pathways in the environment and, potentially, for investigating their biological effects on marine organisms. They provide tools also to investigate sea resources, oceanographic processes and marine contamination on a quantitative basis and at the same time address the problems of coastal zone management. Although other approaches can be used to obtain information about the isotopic composition of elements, mass spectrometric techniques clearly dominate the field of isotopic analysis. The identification of sources of environmental contamination can be done by an isotopic abundance and/or an isotopic ratio analysis. Once the different sources are identified, the isotopic abundances and the isotopic ratios can be used to quantify the contribution of each source by source apportionment. Isotopic signatures are the basis for investigation of historical and environmental changes of the examined sampling sites.

Accurate analytical methodologies for plutonium, uranium and thorium based in sea water on the application of High Resolution ICP-MS in parallel with solid metrological concepts (uncertainty, traceability and validation) were developed in this study. Usually long lived radionuclides are present at trace levels in the open ocean and cannot be measured directly; therefore they must be separated from a wide range of sample components, and additionally preconcentrated.

Several methods for sample preparation, separation and preconcentration of the analytes of interest, based on solid-phase extraction (SPE) with nano materials and chelate resins were investigated and applies. High resolution mode of ICP-MS measurements were used for quantitative determination of plutonium, uranium, thorium in the open ocean and alternatively as a tool for studies on the isotopic fractionations during the sample preparation process isotopic ratio analysis. Isotopic signatures were used for investigation of environmental changes in several sampling sites.

Obtained in this study results represent an important step in the identification and enhancement of our understanding of the pollution sources in the open ocean.

POSTER 2 - ENV: 6

Topics: Environmental sciences

Keywords: plastic wastes, mercury, pollution

COMPARATIVE STUDY ON THE EFFECT OF ULTRA-TRACE MERCURY IN PLASTIC WASTES IN THE KUWAIT BEACHES

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Recent years witnessed plastic wastes in the coastal waters and shoreline beaches. Plastic wastes classified by light and heavy density polyethylene (LDPE and HDPE) materials physically obstructed marine lives. Evidences were least, indicating mercury (Hg) concentrations in the plastic wastes as a long-term pollutant in the ecosystem and hence, chosen the study. Mercury loss or accumulation, low level detection and matrices instability was observed when different methods were used to detect the Hg levels. However, this study achieved repeatable and reproducible results following the micro-analytical methods, digestion of solid samples to liquid state and samples analysis in the direct mercury analyzer (DMA-80) with absorption spectrophotometry (0.0015ng detection limits). Annually, quantification and dispersion of plastic wastes in beaches not only destroyed the aesthetic value of the beaches but also characterized the additive source of Hg contamination in plastics that claimed many marine lives.

POSTER 2 - ENV: 7

Topics: Environmental sciences

Keywords: ICP-OES, flow-injection analysis, sample preconcentration

Magnetic nanoparticles coated with ionic liquid for the pre-concentration of Pb in drinking water and the subsequent quantification by FI-ICP-OES

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There is no doubt on toxicity of lead and its harmful effects on human health. Besides, widespread use of Pb by industry has led to enormous exposure of environment including water, soil and air. Accordingly, careful control of Pb level in environment is necessary. Inductively coupled plasma optical emission spectrometry (ICP-OES) is a technique frequently applied for the analysis of environmental samples. However, the use of ICP-OES for the determination of Pb is hampered by the poor sensitivity for this element. Thus, assessment of naturally occurring lead levels in environmental samples is impossible without a preliminary pre-concentration step.

In this contribution an innovative procedure for the analysis of Pb in aqueous sample solutions is presented. The approach is based on the enrichment of Pb using the concept of dispersed particle extraction (DPE), followed by automated separation and slurry ICP-OES analysis of the analyte containing sorbent particles using a flow-injection procedure. Silica coated magnetic Co-nanoparticles covered with a layer of ionic liquid (IL) which acts as cation exchanger (Co2O3@SiO2@[P66614][BEHPA]) were used as sorbent material. For sample analysis the magnetic particles were suspended in the sample solution. After analyte adsorption the suspension is directed through a magnetic trap; thereby, the analyte containing magnetic nanoparticles are retained and efficiently separated from the sample solution. After a washing step, the magnetic field of the trap is switched off, and the released particles are transported towards the ICP-OES using a carrier solution. To improve reproducibility and sensitivity of analysis sample enrichment and measurement have been performed using a Flow-Injection procedure which has been coupled online to the detection system. In an application example, the proposed FI-ICP-OES procedure has been successfully used for the quantification of lead in drinking water.

POSTER 2 - ENV: 8

Topics: Environmental sciences

Keywords: APM, real-time-monitoring, volatile elements, ICPMS

Measurement of elements in airborne particulate matter: comparison between real-time monitoring data and filter-collection data

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Introduction

It is necessary to monitor airborne particulate matter (APM) in terms of public health. Previously, we carried out a long-term monitoring of APM by filter-collection method with a 3-stage Andersen sampler. Analyses with inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma optical emission spectrometry (ICPOES) were conducted from 1995 to 2013 in Tokyo, and revealed that elemental composition in APM is altered dependent on the particle size and sources [1]. In that previous research, the average data for one month were obtained. To obtain a high-resolution monitoring data, we developed the system of real-time monitoring of APM, which enables the direct analysis of APM and the short-term monitoring (every 5 minutes) of elemental composition in APM [2]. However, we found that there was difference in quantitative values of volatile elements, such as selenium (Se), arsenic (As) and antimony (Sb), between the real-time monitoring data and the filter-collection data. In this study, we tried to investigate the cause of differences in the quantitative values of these volatile elements.

Experimental

In real-time monitoring, APM was analyzed with 5-min interval for 1, 3 and 7 days. APM with size < 1 μm was directly introduced into ICPMS through a gas exchange device (GED), in which gas molecules were exchanged from air to argon. The element concentrations in APM were calculated using an ultra sonic nebulizer (USN) with a desolation system. In filter-collection method, APM was collected with a 0.025 mm filter. Recovery rates were defined as follows: quantitative value obtained by real-time method/ quantitative value obtained by filter-collection method. SbH_3 gas was generated by the reaction of 1 ppm Sb with 1.5% sodium borohydride（$NaBH_4$）and introduced into a gas to particle conversion device (GPD). The resulting SbH_3 particles were used as artificial APM. Different sizes of artificial APM (<0.14, 0.14-0.32, 0.32-3.7, 3.7< mm) were sampled using a 13-stage Andersen sampler.

Results and Discussion

The quantitative values of Se, As and Sb in real-time monitoring were significantly higher than those in filter-collection method, and the recovery rates of those volatile elements were 319%, 169% and 164%, respectively. Then, we hypothesized that the cause of abnormal recovery rates observed in volatile elements was as follows; (1) tiny particles, in which volatile elements were enriched, were not collected on filters, or (2) volatile elements existing as gas were not collected on filters. We then generated artificial APM (SbH_3 particle) and filtered them with a 13-stage Andersen sampler. As a result, the most abundant particles were collected on a filter with < 0.14 mm, suggesting that tiny particles, in which volatile elements were enriched, were missed in filter-collection method.

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POSTER 2 - ENV: 9

Topics: Environmental sciences

Keywords: Gaseous mercury (Hg) in ambient air, Direct analysis and real-time monitoring, Gas to particle conversion device (GPD), Gas exchange device (GED), Inductively coupled plasma mass spectrometry (ICPMS)

Direct analysis of gaseous mercury in ambient air by inductively coupled plasma mass spectrometry coupled with gas to particle conversion-gas exchange technique

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It is well known that mercury (Hg), especially for methylmercury (MeHg) and dimethylmercury (DMHg), is a highly toxic pollutant that possesses a serious threat to human health such as Minamata disease as well as wildlife. Gaseous elemental Hg (GEM, Hg^0), reactive gaseous Hg (RGM, Hg^{2+}) and particulate Hg (Hg_p) are known as atmospheric Hg and former two exist mainly (>95 %) in the gaseous phase. The GEM is a dominant form of gaseous Hg in the atmosphere with background levels reported from 1.0 to 1.7 ng m^{-3} and from 0.5 to 1.2 ng m^{-3} in the Northern and the Southern Hemisphere, respectively. In Japan, the guideline value has been set for hazardous air pollutants to reduce health risk since 1996 and the value is less than 40 ng m^{-3} for annual average on Hg and its compounds. In addition, the Minamata convention on Hg was unanimously adopted in Minamata city, Kumamoto prefecture, Japan in October 2013, and signed by 92 nations including Japan. From these points of view, atmospheric gaseous Hg (GEM and RGM) should be measured frequently to monitor the concentration of Hg in atmospheric environment as well as working and living environments. In order to estimate the risk concerned with respect to the working and living environments from gaseous Hg, direct and high sensitive analysis as well as real-time monitoring of gaseous Hg in ambient air is ideally required. However, the current analytical techniques for gaseous Hg are not direct one.

An inductively coupled plasma mass spectrometry (ICPMS) is expected as an effective analytical tool for the direct analysis of gaseous Hg, since it is widely accepted for trace element analysis due to its high sensitivity, multielement capability and wide linear dynamic range. In our previous study, direct and high sensitive analysis of ultra-trace metallic compound gas such as $Cr(CO)_6$, $W(CO)_6$ $Mo(CO)_6$, AsH_3 and PH_3 was newly proposed and its figures of merit were successfully demonstrated by ICPMS coupled with gas to particle conversion-gas exchange technique (GPD-GED-ICPMS).[1,2]

In the present study, we applied the GPD-GED-ICPMS to the direct analysis of gaseous Hg in ambient air and succeeded the direct detection of it at the concentration level of a few ng m^{-3} in ambient air for the first time in the world. The signal stability as well as limit of detection (LOD) of gaseous Hg in ambient air were examined.

References:

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POSTER 2 - ENV: 10

Topics: Environmental sciences
Keywords: flow injection, flame atomic absorption spectrometry, salinity, seawater, Zn

Determination of Dissolved Trace Zn in Seawater with Different Salinity by flow injection second gas induction elution method with Flame Atomic Absorption Spectrometry

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A high speed separation and preconcentration in a knotted reactor coupled with flame atomic absorption spectrometry was developed for the determination of dissolved trace Zn in seawater with different salinity. This new method based on the flow injection (FI) on-line preconcentration procedure in a knotted reactor using second gas induction elution method coupled with flame atomic absorption spectrometry (FAAS). The preconcentration flow rate was 6.0 mL/min, preconcentration time was 60 s. When the 20μg/L Zn solution was detected, the EF was promoted from 9.4 to 22.5 compared with the traditional method; The detection limit(3σ) was 0.34μg/L for Zn; The sample throughput was 28/h, and The relative standard deviation(RSD, n=11) was 2.3% for Zn. The method has been applied to the determination of dissolved trace Zn in seawater with different salinity with the recovery from 94.6% to 97.1% and can satisfy the determination requirements of dissolved trace Zn in seawater with different salinity at river mouth.

POSTER 2 - ENV: 11

Topics: Sample introduction and sample preparation, Elemental analysis, Environmental sciences
Keywords: Auto-Dilution, ICP-OES, SDX HPLD, Wastewaters

Utilising Prescriptive and Intelligent Dilution for the High Throughput Analysis of Metals in Wastewaters

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Wastewaters are required to undergo several different treatment processes to reduce the concentration of toxic metals to safe levels before being allowed to reenter the ecosystem. In order to manage the treatment process statutory water authorites, such as Thames Water, routinely analyse wastewaters from its treatment plants. The concentration of metals within these samples usually varies by several orders of magnitude, which without prior dilution, can saturate detectors within ICP-OES systems and hinder the reporting of the results. In order to address this issue time consuming manual dilutions were required to be conducted prior to analysis. However, now the newly devleloped SDX High Performance Liquid Dilution (HPLD) system can carry out prescriptive dilutions and also intelligently redilute samples back into a calibration range which removes the need for re-running samples and time and labour intensive manual dilutions.

Teledyne CETAC's SDX HPLD system was utilised in conjunction with a Thermo Fisher Scientific iCAP 7400 ICP-OES (Hemel Hempstead) to generate concentration data for 15 wastewater samples and 3 standards provided by Thames Water. A stock multi element standard was created of Al, B, Ba, Be, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Sr and Zn so that a calibration line could be created by utilising the prescriptive dilution capability of the SDX QTEGRA plug-in. The analysis utilised three different dilutions of 100X, 20X and 10X from the stock standard to form the calibration line. Yttrium and Iridium was introduced online as an internal standard. Samples which suppressed the signal of the internal standard below 75% and above 125% were re-diluted in 10X increments until the internal standard signal was brought back into range. Any sample with elemental concentrations above the concentration of the top standard in the calibration line was intelligently re-diluted so that the signal would correspond to 60% of the intensity of the top standard.

POSTER 2 - ENV: 12

Topics: Elemental analysis

Keywords: fertilizer, rare-earth element, ICP-MS, high matrix introduction, aerosol dilution

DETERMINATION OF Ce, Eu, Gd, La, Sm AND Yb IN MINERAL FERTILIZER BY ICP-MS

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Usually, inorganic fertilizers are derived from phosphatic rocks that are a source of macro and micro nutrients. Furthermore, raw materials derived from industrial residues have been added to fertilizer in order to complement the micronutrient content. The growing in REEs recent applications lead to increase the interest in its determination in various matrices.Thus, the aim of this study was to propose method for the determination of La, Ce, Eu, Gd, La, Sm, and Yb in mineral fertilizer by ICP-MS. About 150 mg of samples were digested in a high temperature and pressure microwave oven (Ultrawave, Milestone), using diluted sulfuric acid (3 mL of H_2SO_4 + 3 mL of H_2O) and the following heating program: temperature = 250°C; ramp = 20 min; hold = 30 min. Digested samples were diluted to 15 mL and centrifuged. Supernatants were diluted 50 times and analyzed by ICP-MS (Model 7900, Agilent). The high content of matrix elements in digested solutions may cause transport problems during ions sampling into MS and isobaric interferences.Thus, a robust analyses condition should be employed to improve high dissolved solids tolerance. Therefore, the Octapole Reaction System was operated in collision mode, using He flow of 10 mL min^{-1} and discrimination energy of 7V to reduce polyatomic interferences. Furthermore, aerosol dilution by a High Matrix Introduction (HMI) accessory was employed using an Ar additional flow of 0.5 L min^{-1} to sample nebulization argon flow. The isotope ^{105}Pd was used as internal standard for the determination of ^{139}La, ^{140}Ce,^{146}Nd, ^{147}Sm, ^{153}Eu,^{157}Gd e ^{173}Yb. A standard reference material of marine sediment (SRM® 2702 - NIST) was used to accuracy evaluation.Comparing the obtained results to certified values, relative errors ranging from -15% to -5% were obtained.The results obtained for mineral fertilizer were La142±6, Ce253±9, Nd; 117±3, Sm20.3±0.4, Eu5.8±0.2, Gd18.7 ±0.3 and Yb3.68± 0.02. Addition and recovery test ranged from 100% to 107%.

POSTER 2 - ENV: 13

Topics: Sample introduction and sample preparation, Environmental sciences
Keywords: drinking water, sampling, stabilization, trace analysis

Stabilization of potable water containers with silver ions in emergency situations - challenges for sampling and analysis

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According to the Austrian drinking water regulation, potable water can be packed and stored for emergency situations. Since the containers need to be prepared prior to any occurring emergency situation, the microbiological conservation is a major issue. One legally permitted approach is the use of silver, which can be added to potable water in several ways like solid (as a pellet), liquid or by electrolysis. The treated water could be prepared in or taken from plastic bottles, metal cups or metallized dispenser bags. The concentration of silver ions in the water is crucial for storage stability and therefore needs to be determined accurately. However, sampling is a relevant factor in error control. Different surfaces and storage periods may influence the amount of recovered silver and different extraction parameters may be needed to access all present silver ions, which may stick to the containers' surface. Also, the initial water quality (hardness, disinfectants) can impact the effectiveness of silver addition.

In this contribution the three previously mentioned addition methods of silver ions are compared and challenges of sampling and analysis are investigated. Different methods, namely AAS, ICP-OES and ICP-MS, were evaluated regarding sensitivity and reproducibility at target analyte concentration (8 ppb, according to Austrian regulations). Finally, parameters are given to combine reliable sampling with an accurate analysis technique to ensure the required concentration of silver ions, best water quality and maximum storage life.

POSTER 2 - ENV: 14

Topics: Environmental sciences

Keywords: ICPMS, water treatment, drinking water, ozone, sodium hypochlorite

Investigation of the speciation change of chlorine, bromine and iodine in the process of advanced water treatment in a public water treatment plant

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Introduction

In recent years, an advanced water treatment system has been employed in public water treatment plants in Tokyo. Ozone and sodium hypochlorite solution (NaOCl) are mainly used in the advanced water treatment system [1]. However, ozone and NaOCl have high reactivity with organic compounds and cause the contamination ofdisinfection by-products (DBPs) in drinking water [2]. In addition, it is unknown that which steps of water treatments cause the generation of those DBPs in advanced water treatment. In this study, we investigated the speciation change of chlorine (Cl), bromine (Br) and iodine (I) in the process of advanced water treatment in a public water treatment plant.

Experimental

Water samples were collected at eight spots of the advanced treatment process in a public water treatment plant (①raw water, ②pre-stage sand filtration treatment, ③coagulating sedimentation treatment,④ozone treatment,⑤biological activated carbon treatment, ⑥pre-chlorine treatment, ⑦post chlorine treatment and ⑧drinking water). The samples were pre-concentrated by lyophilization. Total concentrations of Cl, Br and I were determined using inductively coupled plasma mass spectrometry (ICPMS) and the speciation analysis of Cl, Br and I was conducted using ion chromatography (IC) -ICPMS with an anion exchange column.

Results and Discussion

Total concentration of Cl in raw water and drinking water were 14.8 mgL^{-1} and 17.1 mgL^{-1}, respectively. IC-ICPMS analysis revealed that the increasing Cl level in drinking water attributed to the increases of Cl^- and ClO_3^-, which are derived from NaOCl used in the pre-chlorine treatment (⑥). Total concentrations of Br in raw water and drinking water were 40.1 μgL^{-1} and 44.1μgL^{-1}, respectively. IC-ICPMS analysis revealed that 99% of Br in raw water was present as Br^-, while 26% of Br was present as Br^- and BrO_3^- and more than 70% of Br was derived from unknown Br compounds produced in the pre-chlorine treatment (⑥). This suggests that NaOCl mediates the generation of unexpected Br compounds. Total concentrations of I in raw water and drinking water were 9.0 μgL^{-1} and 6.4 μgL^{-1}, respectively. I^- concentration in raw water (1.6 μgL^{-1}) was higher than that in drinking water (0.1 μgL^{-1}), while IO_3^- concentration in raw water (0.8 μgL^{-1}) was lower than that in drinking water (4.9 μgL^{-1}). I^- level decreased and IO_3^- level increased in the ozone treatment (④). These results suggest that the increased IO_3^- level in the advanced water treatment system is due to the oxidation of I compound in the ozone treatment (④).

References

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POSTER 2 - ENV: 15

Topics: Sample introduction and sample preparation

Keywords: Cadmium, mercury, lead, magnetic solid-phase extraction, zeolite, iron oxide magnetic nanoparticles, inductively coupled plasma optical emission spectrometry

Magnetic solid-phase extraction using ZSM-5 zeolite/Fe2O3 as a sorbent for determination of cadmium, mercury and lead in urine samples prior to inductively coupled plasma optical emission spectrometry

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Magnetic solid-phase extraction (MSPE) has recently received great interest since it reduces sample preparation time and facilitates sorbent manipulation. In MSPE, the magnetic sorbent is dispersed into the aqueous phase and after extraction, it is easily separated from sample solution by applying an external magnetic field, and thus avoids time-consuming filtration or centrifugation steps for phases separation. Next, target analytes can be eluted using a proper solvent for further determination.

Zeolites are aluminosilicate materials that exhibit well-defined highly porous structures. The general zeolite structure is a three-dimensional network of repeating isomorphous SiO_4 and AlO_4^- tetrahedra linked by oxygen atoms. Their anionic framework makes zeolites natural cationic exchangers while their well-defined pores lend some degree of preference to the ions adsorbed.

The purpose of this work is to present a simple MSPE method, employing a composite based on ZSM-5 zeolite decorated with iron oxide magnetic nanoparticles (i.e., ZSM-5 zeolite/Fe_2O_3) presented as a valuable sorbent, for the simultaneous separation and preconcentration of Cd, Hg and Pb in urine samples for subsequent measurement by inductively coupled plasma optical emission spectrometry (ICP-OES).

The method has been evaluated under optimized extraction conditions obtaining a linear range from 5 to 100 μg L^{-1} (r=0.998, N=7) for Cd and Hg, and from 10 to 100 μg L^{-1} (r=0.999, N=6) for Pb. The repeatability of the method has been evaluated at a 50 μg L^{-1} spiking level obtaining coefficients of variation between 4 and 5% (n=6). Limits of detection have been 0.4 μg L^{-1} for Cd, 0.1 μg L^{-1} for Hg and 2.1 μg L^{-1} for Pb. These values satisfy the threshold limit established by the Ministry of Labour and Social Affairs (Spain) for normal content of these metals in human urine (i.e., 3.4 μg L^{-1} for Cd, 10 μg L^{-1} for Hg and 85 μg L^{-1} for Pb). Finally, trueness has been assessed analyzing spiked urine samples obtaining relative recoveries values ranged between 95% and 108%.

On the whole, it is important to point out that this composite has been employed in MSPE for the first time and presents remarkable advantages such as high extraction efficiency, low cost, simple synthesis and easy manipulation under a magnetic field. On the other hand, the proposed method avoids acid digestion of urine samples resulting in a more environmentally friendly procedure and reducing risk of analyte losses (i.e., Hg).

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Innovation (project n. CTQ2011-23968), Generalitat Valenciana (Spain) (projects n. GVA/2014/096 and PROMETEO/2013/038) for the financial support. P. Baile also thanks Ministry of Education for her FPU grant (FPU14/04589).

POSTER 2 - ENV: 16

Topics: Elemental analysis

Keywords: gallium, natural waters, reaction cell ICP-MS

ICP-QQQ for low level gallium analysis in natural waters

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Gallium has been used as a proxy for aluminum in studies of watershed weathering dynamics. Gallium is usually present at low ng/L level in natural waters and both Ga isotopes 69 and 71 have significant isobaric interferences from Ba^{2+} and MnO respectively, and thus have required analysis by sector field ICP-MS in medium resolution mode and/or chemical removal of interfering ions prior to analysis. Quadrupole ICP-MS analysis using reaction gases provides an alternative to medium and high resolution. In this study an Agilent 8800 ICP-QQQ was used in H_2 and NH_3 modes to remove MnO and Ba^{2+} interferences at Ga m/z 71 and 69 respectively. Using hydrogen as reaction gas the MnO interference at 71 is essentially eliminated and detection limits for Ga at m/z 71 are < 1 ng/L. Double charge interferences are more difficult to deal with. Ba^{2+} interference is largely unaffected by H_2 or NH_3 at m/z 69 (i.e. Q1 and Q 2 at m/z 69); however, monitoring mass shifted adducts showed that 3.8% of Ga ions form the +17 adduct at m/z 86 whereas only 0.005% of Ba^{2+} ions are mass shifted. Detection limits for Ga under these conditions are ca. 7 ng/L and Ba^{2+} interference in the presence of 500 µg/L was not significantly different than the blank.

POSTER 2 - GDMS: POSTER SESSION 2: Glow discharge mass spectrometry

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com SOUTH HALL

POSTER 2 - GDMS: 1

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Glow discharge mass spectormetry

Keywords: Matrix matched Standard preparation, Lithium Ion Battery

Calibration Approaches in Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Sector Field Glow Discharge-Mass Spectrometry (SF-GD-MS)

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One postulated cause of the degradation of Lithium Ion Batteries (LIBs) is assigned to the passivation layer on the negative electrode which is formed during the first cycle due to high reductive potentials. This passivation layer is called Solid Electrolyte Interphase (SEI) and grows with ongoing cycling and consumes active lithium which results in capacity losses. Furthermore, the dissolution of transition metals - originating from the positive electrode – was proposed to have an influence on the SEI as it affects the surface of the passivation layer.[1] The conventional method to examine passivation layers in battery research is the use of X-ray Photoelectron Spectroscopy (XPS) which suffers from poor depth resolution as well as long measurement times due to small sample spots as well as the low sample throughput.[2]

Due to a lack of reliable methods for micrometer scale determination of the elemental distribution in aged lithium ion electrodes, standard electrodes for the calibration of plasma based depth-and spatially-resolved analysis like Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Sector Field-Glow Discharge-Mass Spectrometry (SFGDMS) were developed. The solid electrode sample was investigated using a 193 nm ArF Excimer Laser with spot sizes ranging from 2.5-150 µm and subsequently analyzed with ICPMS as well as with pulsed GD sources using high resolution mass spectrometry.

Considering the cathode/anode active material combination of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) and graphite as a standardized and well-known setup for LIB[3], the synthesized NCM/graphite composite allows to quantitatively study the manganese content in a low micrometer range on the surface and inside the bulk material of the anode.

In order to examine the effect of SEI growth and transition metal deposition on negative electrodes, the two plasma based methods are promising tools for the direct analysis of these layers.

In this work, self-prepared standards are used to calibrate the LA-ICP-MS and SFGD-MS externally on typical elements in the LIB (lithium and manganese) relating to the complex matrix. The validation was performed via bulk analysis of the element spiked electrodes using ICPOES.

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POSTER 2 - GDMS: 2

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Glow discharge mass spectormetry
Keywords: SiC, laser ablation, GD-MS, impurity

Determination of trace elements in silicon carbide wafers using GD-MS and LA-ICP-MS

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Trace impurities such as B, Al, Ti, V, Fe, Cu in high purity silicon carbide (SiC) wafers were determined by fast flow glow discharge mass spectrometry (GD-MS) and laser ablation inductively coupled plasma spectrometry (LA-ICP-MS). The conducting n-type SiC wafers were measured by fast flow GD-MS and LA-ICP-MS. The glow discharge source current and argon gas flow parameters were 30 mA and 400 mL/min, respectively. The quantification results of the GD-MS measurements were calculated by corrected relative sensitivity factors (RSFs) using Fe-base certified reference materials. The laser ablation system consists of a 213 nm Q-switched Nd:YAG laser. For the laser and gas set-ups, signals of single-spot ablation were recorded with a pulse rate of 20 Hz with Helium carrier gas. The elements concentrations by LA-ICP-MS were calculated by semi-quantitative calibrations using a glass NIST 612 as the semi-quant standard. LA-ICP-MS results agreed well with the results of GD-MS. GD-MS and LA-ICP-MS have a good performance for rapid multi-element analysis of high purity SiC wafer under the mg/kg levels. GD-MS and LA-ICP-MS allow the characterization both in bulk and in spatially resolved analysis.

POSTER 2 - GDMS: 3

Topics: Glow discharge mass spectormetry

Keywords: Glow Discharge Mass Spectrometry, Calibration, Relative Sensitivity Factors

Matrix Independent Calibrations in Glow Discharge Mass Spectrometry

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Glow discharge (GD) based techniques and in particular GD mass spectrometry (GD-MS) are powerful tools able to determine low mass fractions of analytes in different materials providing fast and sensitive multi-element determination without laborious sample treatment/preparation. As many other analytical techniques, GD-MS requires calibration of the signal response for accurate quantification. Therefore, the lack of matrix matched certified reference materials is a very limiting point for the accurate determination of trace and ultra-trace impurities. Multi-matrix calibrations are also possible in GD-MS but the measured intensity strongly relies on the sputtering rate (q_S) which depends on the material and discharge condition. In addition, the application of the concepts of relative sensitivity factors (RSF) and standard relative sensitivity factors (StdRSF) could provide good approximations, especially for high purity substances. However, the sensitivity depends on the sample matrix and the discharge conditions. Further studies about the effect of these parameters are necessary to understand the variations of the relative sensitivity and to select suitable working parameters.

Different quantification approaches were evaluated aiming to obtain an improved matrix-independent quantification approach adequate for the determination of metallic impurities in the trace range (uncertainty of 15% on the individual impurities). These investigations were carried out using the fast flow source GD-MS instrument (ELEMENT GD). The effect/impact of the discharge conditions (voltage, current, discharge gas pressure/flow) on the sensitivity was evaluated using reference materials with Al, Cu and Zn matrices containing traces of various metallic elements.

In addition, the possibility of a multi-matrix calibration of oxygen in GD-MS was investigated using a set of new conductive samples containing oxygen in the mass percent range of concentration in three different matrixes (Al, Mg and Cu) produced by a sintering process. Discharge parameters were optimized for the generation of reproducible background and signal intensities of non-metals. The matrix specific RSFs and limits of detection were determined under these conditions.

This work was conducted within the EMRP project SIB09 ELEMENTS. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

POSTER 2 - GDMS: 4

Topics: Glow discharge mass spectormetry

Keywords: GD-MS, fast flow, pulsed, RSF, calibration

Calibration factors in Fast Flow Glow Discharge Mass Spectrometry (FF-GD-MS): Continuous vs. Pulsed Mode

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Sector field glow discharge mass spectrometry is applied for the analysis of high purity metals, alloys, semiconductors and ceramics, especially by the aerospace, electronics and photovoltaic industries.

The Thermo Scientific™ ELEMENT GD™ PLUS GD-MS features a fast flow glow discharge source that can be operated in continuous or pulsed mode. For the traditional GD-MS market of analyzing bulk metals and alloys, continuous mode operation offers the advantage of higher sputter rates to remove surface contaminations quickly. Also, the set of calibration factors (RSF = Relative Sensitivity Factor), which is widely applied for semiquantitative analysis, is based on continuous mode operation.

The pulsed mode of the glow discharge source results in enhanced overall stability and widely adjustable source parameters with minor influence on the elemental ratios analyzed. It has been shown earlier that semiquantitative results obtained with pulsed mode typically yield accuracies within a range of ±30%, using the general calibration table based on continuous mode results. With the wider use of pulsed mode operation, a more detailed investigation on calibration factors is necessary.

In order to facilitate the use of both modes in routine analytical laboratories, the calibration factors have been re-visited to further evaluate the accuracies and the overlap between continuous and pulsed mode operation.

POSTER 2 - GDMS: 5

Topics: Glow discharge mass spectormetry

Keywords: Ambient MS, DBDI, Plasma, Soft-Ionization, Direct analysis

SICRIT Mass Spectrometry: Simple, Smart and Sensitive

Jan-Christoph Wolf[1], Klemens Maria Thaler[2], Klaus Wutz[1], Christoph Haisch[2], Reinhard Niessner[2]

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Soft ionization by chemical reaction in transfer (SICRIT) directly merges the atmospheric pressure inlet of a mass spectrometer with a small and rigid dielectric barrier discharge based plasma ionization source. This significantly enhances ion transmission into the MS and thereby the sensitivity. Although the whole sample passes the plasma, the ionization process is very soft usually yielding solely MH^+ analyte species. As a further advantage the source does not need any additional gas or liquid supplies and can be attached to virtually any existing atmospheric pressure inlet MS interface. Several studies were conducted on various instruments including a LCQ DECA X, LTQ XL, LTQ Orbitrap XL and Orbitrap Exactive all from Thermo Scientific, an AB SCIEX 3200 QTRAP, a Synapt G2 from Waters, and a portable miniature mass spectrometer MINI 10.5 from Aston Labs. All instruments were fitted with the SICRIT source. In some studies, the source was directly coupled to chromatographic analysis systems including a nano-LC (pesticides analysis), a LC (CWA analysis), a GC (forensic analysis) and a laser ablation system (PAH analysis).

The source has proven to be capable of efficiently ionizing a wide range of substance classes including chemical warfare agents (CWA), alcohols, PAH, pesticides, and polymers. Due to its flow-through design it can be used for direct analysis without any sample pretreatment or in combination with e.g. LC, GC, SPME or laser ablation.

The general sensitivity for most compounds (e.g. CWA, pesticides, illicit drugs) was found to be in the ppq/low ppt range. Actually for some applications absolute detection limits were found to be as low as 20 fg, mainly depending on the MS-instrument used. For direct gas phase analysis, the linear dynamic range usually spans more than three orders of magnitude. This can be enhanced up to six orders of magnitude by coupling with chromatography.

Mechanistic studies showed an atmospheric pressure chemical ionization (APCI) related ionization mechanism, however negligible fragmentation was observed compared to classic APCI. By means of SICRIT-Orbitrap-MS we were able to directly identify more than 100 known and many yet unknown aroma compounds in the smell of one single coffee bean within one second of measurement, without any sample pretreatment.

Our results show that the SICRIT ionization source is very sensitive and versatile. It can be used either directly for screening or in-field-applications or as interface to any chromatography or sample delivery system. It is applicable for a very broad range of substance classes and enables new ways of analysis. It`s a "one for (almost) all" ionization source.

POSTER 2 - ISO: POSTER SESSION 2: Isotope ratio analysis

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com SOUTH HALL

POSTER 2 - ISO: 1

Topics: Isotope ratio analysis, Environmental sciences

Keywords: provenancing, caviar, strontium, isotopes, isotopic pattern deconvolution

Tracing the origin of the “black gold”: Elemental and isotopic pattern of sturgeon caviar and the influence of water, feeding and processing

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Sturgeon caviar is one of the most expensive food commodities. While farming of sturgeons for caviar production is emerging, there is still a decrease in natural populations due to illegal fishing. As a consequence, sturgeon caviar trade has been put under international regulations. However, the control of the origin of sturgeon caviar is still a challenge. Sound analytical methods like elemental and isotopic fingerprinting have high potential for the unambiguous determination of the origin of sturgeon caviar.

In principle it is expected that the elemental pattern and the $^{87}Sr/^{86}Sr$ isotope ratio of water of a specific habitat (fish farm vs. natural environment) is reflected in the caviar. However, feeding of fish but also salting of caviar can have a potential influence on its chemical signature.

In this pilot study therefore untreated caviar, processed caviar (i.e. salted), fish feed, salt and water from six sturgeon farms (one in Austria, four in Italy and one in Iran) were investigated for their elemental and $^{87}Sr/^{86}Sr$ isotopic composition using (multi collector) inductively coupled plasma mass spectrometry ((MC) ICP-MS). Due to the complex matrices, detailed analytical procedures for sample preparation and measurement needed to be developed.

The first results showed that fish farms from geologically different areas could be differentiated by combining the elemental and isotopic signature of water. Moreover, the signature of these fish farms was different from the water signature of the natural living habitat of the wild sturgeon in the Lower Danube and the Southern Caspian Sea. The information of the water could also be found in the untreated caviar even though a distinct influence of the fish feed (with an elemental and $^{87}Sr/^{86}Sr$ ratios suggesting marine origin) could be observed in caviar from fish farms. Nonetheless, the majority of the caviar samples from fish farms could be distinguished from the Danube and Caspian Sea water taken as reference for caviar potentially harvested from wild sturgeon. Salt significantly changed the chemical fingerprint of the processed product. The original isotopic composition of the raw caviar could however be well determined using isotopic pattern deconvolution.

A fully validated analytical protocol for identifying the original $^{87}Sr/^{86}Sr$ isotope ratio and elemental composition of processed caviar has great potential to act as a new tool in caviar provenancing.

POSTER 2 - ISO: 2

Topics: Isotope ratio analysis, Archaeometry and forensics

Keywords: Strontium isotopy, archaeology, Bronze Age, 87Sr/86Sr

The application of Sr isotope ratios to study human migration in the late Bronze Age in Stillfried/March (AT)

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The human depositions of Stillfried/March (Lower Austria, Austria) were found in trapezoid storage pits located in the hillfort site associated to the late Urnfield Period (late Bronze Age). Some archaeological and anthropological findings indicate to those depositions being cultic in origin. As the name 'Urnfield' already presumes the custom mode of funerary for this time period was to cremate the dead and to bury the urns containing their ashes in urnfields. Such urnfields can also be found near the settlement of Stillfried/March [1]. This leads to the question, of the identity of those deposited individuals that were treated differently to those who were buried in the urnfields. One of the theories is an allochthonous residential background. In the course of the project 'Resource management, power and cult in Stillfried?' (FWF P28005) this question, amongst others, gets investigated [2].

Strontium isotopic analyses of incorporated environmental signatures in human and animal remains have been a key tool to investigate migration and residential changes in archaeological and anthropological contexts since material diffusion or diffusion of knowledge is no definite proof for migration. Hence, multi-element and $^{87}Sr/^{86}Sr$ isotopic analyses of archaeological human and animal tooth samples as well as archaeological mollusc shells were performed using ICP-QMS (Perkin Elmer NexION 350D) and MC ICP-MS (Nu Plasma HR, Nu Instruments), according to validated measurement procedures [3]. The determined $^{87}Sr/^{86}Sr$ ratios in tooth enamel (‘archive of childhood’) were compared to those of the secondary dentine (‘recent’ signature). Preliminary results indicate that some of the individuals might have died at different places than they were born, as the $^{87}Sr/^{86}Sr$ ratios show significant differences. For interpretation of autochtony or allochtony of the human depositions, the $^{87}Sr/^{86}Sr$ ratios of all analysed individuals are compared to those assessed in the local proximity (via the establishment of so-called ‘isoscapes’) based on the bioavailable Sr of recent water and soils (NH_4NO_3-extracts) from the surrounding area of Stillfried/March.

[1] Griebl M., Hellerschmid I. (2013). In Müller-Scheeßel N. editor. ‚Irreguläre‘ Bestattungen in der Urgeschichte: Norm, Ritual, Strafe ? Frankfurt am Main: Römisch-Germanische Kommission des Deutschen Archäologischen Instituts. p 327-346.

[2] http://www.orea.oeaw.ac.at/stillfried-ressourcen.html

[3] Irrgeher J., Prohaska T., Sturgeon R. E., Mester Z., and Yang L. (2013). In Analytical Methods 5(7):1687.

POSTER 2 - ISO: 3

Topics: Sample introduction and sample preparation, Elemental analysis, Isotope ratio analysis
Keywords: Strontium isotopes, phosphorites, leaching, seawater composition

Unlocking isotopic and elemental archives in marine phosphorites: a case study from the Precambrian-Cambrian boundary

Jessica Alexandra Stammeier[1], Dorothee Hippler[1], Oliver Nebel[3], Florian Mittermayer[1], Cyrill Grengg[1], Albrecht Leis[2], Martin Dietzel[1]

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Phosphorites are complex marine deposits that occur along passive continental margins, including key horizons associated with the Cambrian Explosion. They represent possible archives for past marine water chemistry and as such a record of continental weathering and changes of environmental conditions throughout Earth´s history. However, unlocking the elemental and isotopic signature of phosphorites requires a careful approach as solid-solution phosphate chemistry is complex, diagenetic alteration is common and intergrowth with carbonates and detrital silicate cargo is frequent.

To decipher the Sr and Mg isotopic record of specific mineral phases in bulk phosphorite, we performed a series of analyses on selected phosphorite samples from the well-preserved section at Koksu in the Karatau Mountain Range, Kazakhstan. Firstly, quantitative elemental distribution images of Sr, Mg and Ca were recorded by electron microprobe analyses (EMPA) using a JEOL JXA-8200 Superprobe, Montan University Leoben. The detailed images of the different phases showed that Sr is predominantly incorporated into phosphate phases (<0.15 wt.%) over carbonaceous matrix (<0.04 wt.%). Subsequently, Sr and Mg isotope and trace element (incl. REE) data were obtained by measuring on a Nu-plasma II MC-ICP-MS and an Agilent 7500cx ICP-MS respectively, at the Central Laboratory for Water, Minerals and Rocks, NAWI Graz. To investigate the respective Sr and Mg isotopic signatures of the different phases, we applied two step acid leaching using 0.05M and 3 M HNO_3. The differences in the $^{87}Sr/^{86}Sr$ isotopic composition between both leachates and the leached residue sample are systematically higher in $^{87}Sr/^{86}Sr$ in leached phases, yet identical within external reproducibility (2σ). Based on our results we conclude that the $^{87}Sr/^{86}Sr$ of the phosphorites is best represented by the 3M HNO_3 leachate to capture phosphate-carbonate phases representative for authigenic Sr and avoid leaching of the detrital silicate cargo with distinct radiogenic $^{87}Sr/^{86}Sr$ isotopic composition. The whole sequence of our Kazakh phosphorite samples was treated in this manner and record a $^{87}Sr/^{86}Sr_{3M\ leachate}$ isotopic composition of 0.7086-0.7101 that generally resembles the range of published Cambrian seawater. We conclude that our phosphorite samples from Kazakhstan present a valuable archive of Cambrian Sr seawater composition.

POSTER 2 - ISO: 4

Topics: Sample introduction and sample preparation, Isotope ratio analysis
Keywords: strontium, neodymium, isotope analysis, chromatography

Sr and Nd chromatographic separation procedure for precise isotope ratio measurement using TIMS and MC ICP methods-MS

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Rare earth elements (REE) and strontium are well known for their ability to incorporate in ppb concentrations in living bones and teeth, and at higher levels during fossilization. $^{87}Sr/^{86}Sr$ isotope ratios in biogenic apatite can comprise an isotopic fingerprint in provenance and migration studies. Like Sr, Nd isotope composition is an important tracer for taphonomic and reworking processes and is not biased by REE fractionation during diagenesis.

The chromatographic separation of Sr and Nd from apatite matrix is essential for obtaining correct Sr and Nd isotope ratio (IR) results. To reduce IR error and precisely determine Nd concentrations even at ppb level, the isotope dilution (ID) method is widely applied.

The aim of the present study was to develop an analytical procedure for chromatographic separation of Sr and Nd for further $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ IR analysis by MC-ICP-MS and TIMS.

Chromatographic resins were tested with standard multi-element solutions (PerkinElmer) containing 10 mg/L of 44 elements, including REE, Rb, Sr, Ca, etc. Element concentrations for elution curves were obtained by ICP-AES (Optima 8000, major elements) and Q-ICP-MS (ELAN 9000, traces).

SR resin (Triskem) was used for Sr separation. Polypropylene column configuration (D=0.4 cm, h=2 cm, V=250 µL) and elution protocol (7 M HNO_3 and 0.05 M HNO_3) provided effective and complete Sr separation (up to 85%) and purification from Rb and Ca.

For primary REE separation, solutions were loaded on quartz columns (D=0.4 cm, h=2.2 cm, V=300 µL) packed with TRU resin (Triskem). Elution with 1 M HNO_3 and 0.05 M HNO_3 yielded almost 100% REE isolation. Quartz columns (D=0.4 cm, h=2.2 cm, V=300 µL) filled with LN resin were used for further separation of Nd and Sm from the obtained REE fraction.

The approach used for the chromatographic separation resulted in high element yield combined with a low volume of eluate and a small amount of extracted elements thus reducing procedure blanks and sample preparation time.

Nd isotope composition determination was carried out by isotope dilution using a mixed ^{150}Nd-^{149}Sm spike. All measurements were made by MC-ICP-MS (Neptune Plus). The long-term external reproducibility of the Merck Nd standard traceable to SRM NIST Nd_2O_3 gave a $^{143}Nd/^{144}Nd$ of 0.511720 ± 15 (1 SD, n = 40). Normalizing ratio was $^{146}Nd/^{144}Nd = 0.7219$.

Sr fractions were analysed by ID TIMS (Triton Plus) using a mixed ^{85}Rb-^{84}Sr spike. The $^{87}Sr/^{86}Sr$ ratio for NIST 987 standard during the measurement was $^{87}Sr/^{86}Sr = 0.710256 \pm 11$ (1 SD, n=59) with normalizing ratio $^{88}Sr/^{86}Sr=8.37521$.

The described procedure will be applied for Sr and Nd isotope ratio determination in fossil bones from a number of Russian taphonomic settings.

The study was carried out at the “Geoanalytic” Collective Use Centre. Financial support was provided by the Russian Presidential grant for leading scientific schools No. NSh-9723.2016.5.

POSTER 2 - ISO: 5

Topics: Isotope ratio analysis

Keywords: Lead isotope ratios, HR SF ICP-MS, SeaFast system, preconcentration, method validation

Determination of lead isotope ratios in seawater

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The concentration of lead in world ocean surface waters increased significantly owing to industrialactivity and gasoline consumption during last decades. To identify the different pollution sources accurately and to quantify their relative contributions, lead isotope ratios are widely used. Anthropogenic lead in the oceans, derived from high-temperature industrial processes, fuel combustion, and incineration can have an isotopic signature distinct from naturally occurring lead, supplied by rock weathering.

Measurement of ^{204}Pb by ICP-MS is particularly problematic as it is the least abundant of the four stable Pb isotopes and is subject to isobaric interference during analysis from ^{204}Hg. Nevertheless ^{204}Pb isotope is of crucial importance for some geological interpretations. Some studies have dealt with this problem by concentrating analytical efforts on the more abundant and interference-free ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes, but this limits the range of measurable isotopic variability, as much of the natural variation is recorded on $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios. Lead isotopic ratios measurement represents a powerful tool for environmental monitoring of coastal areas as well as in the open ocean.

An analytical protocol for the measurements of isotope ratios in seawater using SeaFast sample introduction system and the Nu Attom Single Collector High Resolution ICP-MS was developed. Due to the high salt content (approximately 3.5% of total dissolved solids) and very low lead levels (approximately 20 pg ml^{-1}), seawater samples require preliminary matrix separation and pre-concentration steps. The pre-concentration/separation step is of crucial importance for decrease isobaric and matrix interferences during measurement step and helps to decrease combined uncertainty on the respective isotope ratios. Several separation procedures were tested, optimised and the remaining matrix concentration carefully investigated.

In order to differentiate between anthropogenic and natural lead sources, both lead concentration and isotopic composition were determined by proposed analytical method. The validation of the method was effectuated according to the ISO-17025 standard. All major sources of uncertainty were identified and propagated together following the ISO/GUM guidelines. The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. The method was applied to the coastal and open seawater samples, collected in different regions of the word.

POSTER 2 - ISO: 6

Topics: Elemental analysis, Isotope ratio analysis, Environmental sciences
Keywords: ICP-MS, MC-ICP-MS, riverine sediment

Investigation of elemental and isotopic fingerprints in riverine sediments from the German Elbe catchment

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Sediments, which represent the memory of an aquatic system, play an important role as indicators for the pollution load of a water body. The Elbe River is one of the major rivers in Central Europe and an important tributary to the German North Sea. In order to evaluate the contaminant load as wells as the contribution of the Elbe to the overall pollution level of this complex ecosystem, reliable analytical methods need to be applied, in particular for distinction between natural background levels as well as anthropogenic inputs.

In this work, distribution maps based on the elemental and isotopic patterns of sediments from the Elbe River were established. For this purpose, the sediments, sampled in 2015, were digested by a microwave-assisted acid digestion using a mixture of nitric, hydrochloric and tetrafluoroboric acid. The elemental composition was quantified by ICP-QQQ-MS in different collision and reaction modes to minimize possible interferences from matrix components.

MC ICP-MS was applied in order to determine isotopic variations of Sr and Pb in the riverine sediments after matrix separation.

Elemental and isotopic data were evaluated along with the determination of total combined uncertainties. ArcGIS® was applied as a tool to compare elemental and isotopic variations along the river to geological and geographical maps and to create distribution maps.

The elemental composition of the sediments varies significantly along the Elbe, which allows prediction of geogenic and anthropogenic contributions in the catchment area. A comparison to data collected 20 years ago for Elbe sediments shows a clear change in concentration level of certain elements (e. g. Sr, Pb, Cd) indicating pollution.

The gained information about the investigated aquatic ecosystem can lead to a deeper understanding of the transportation processes of contaminants and trace contributions to the North Sea from the Elbe River.

POSTER 2 - ISO: 7

Topics: Isotope ratio analysis, Archaeometry and forensics

Keywords: COPPER LEAD AND ANTIMONY ISOTOPE RATIOS, BRONZE AGE ARTEFACTS, MULTICOLLECTOR ICP-MS

MEASUREMENT OF COPPER, LEAD AND ANTIMONY ISOTOPE RATIOS IN 27 EARLY BRONZE AGE ARTEFACTS BY MULTICOLLECTOR ICP-MS.

Jose Ignacio Garcia Alonso, Aida Reguera Galán, Mariella Moldovan, Rosario Pereiro, Lara Lobo

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Three prehistoric copper mines in the northwest of Spain have been recently characterised in terms of their lead isotopic fingerprint [1-3]. It was observed [3] that the isotopic composition of lead in these mines was very different from other ancient copper mines of the Iberian Peninsula, particularly in the south and southwest of Spain, with a pronounced radiogenic profile.

Last year we were able to obtain samples of 27 early Bronze Age artefacts which were found in the northwest of Spain. Impurity analysis revealed that all these artefacts consisted on arsenical copper with only traces of tin. Some of these artefacts were in the form of axes, others in the form of ingots and one was a small sword. Lead isotope ratios were measured both by solution analysis, after the separation of lead from the matrix, and by laser ablation using on-line addition of thallium for mass bias correction, with comparable results. The lead isotopic signature showed that the copper used originated from one or several of the three ancient copper mines described previously [1-3]. However, the discrimination between the three mines was difficult for some of the samples measured. So, copper and antimony isotope ratios were measured in the same samples to gain additional information on the possible source of the copper employed for the manufacture of these artefacts.

The final results and the conclusions obtained from these studies will be discussed in the poster.

[1] G. Huelga-Suarez, M. Moldovan, M. Suárez Fernández, M. Ángel De Blas Cortina, F. Vanhaecke, J. I. García Alonso. Lead isotopic analysis of copper ores from the sierra El Aramo (Asturias, Spain). Archaeometry. 54 (2012) 685-697

[2] G. Huelga Suarez, M. Moldovan, M. Suárez Fernández, M. Ángel De Blas Cortina, J. I. Garcia Alonso. Defining the Lead Isotopic Fingerprint of Copper Ores from North-West Spain: The El Milagro Mine (Asturias). Archaeometry, 56 (2014) 88-101

[3] G. Huelga Suarez, M. Moldovan, M. Suárez Fernández, M. Ángel De Blas Cortina, J. I. Garcia Alonso. Isotopic Composition of Lead in Copper Ores and a Copper Artefact from the La Profunda Mine (León, Spain). Archaeometry 56 (2014), 651-664.

POSTER 2 - ISO: 8

Topics: Isotope ratio analysis

Keywords: Boron, MC-ICPMS, Memory effect, CsCl, NaCl

Experimental evaluation and minimization of memory effect in isotope ratio determination of boron with high resolution multi-collector inductively coupled plasma source mass spectrometry (MC-ICPMS)

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Purpose: The present studies were aimed at the evaluation of memory effect in the measurement of boron (B) isotope ratios ($^{11}B/^{10}B$) with MC-ICPMS. This carry-over effect demands the matching of the concentration as well as the isotope ratio of B in the unknown sample and the standard in standard-sample bracketing (SSB) approach commonly used in MC-ICPMS. Two different wash-out reagents NaCl and CsCl were tested to minimize the boron memory effect. Their optimum concentrations were determined, and their effect on the stability of the boron ion-current was also investigated.

Method: The memory effect was evaluated with the use of a synthetic mixture of boron solution prepared by mixing solutions of enriched ^{10}B, and natural boric acid. The $^{11}B/^{10}B$ isotope ratio in the synthetic mixture was kept about +100 with respect to that in isotopic reference material (NIST-SRM-951). This value of +100 ^{11}B was chosen so as to cover most of the boron solutions encountered in paleo-oceanography and other studies from corals, foraminifera samples, etc. Solutions of NaCl (1% to 10 wt%) and CsCl (1%) were prepared from high purity spec-pure compounds. Thermo-Fisher Neptune MC-ICPMS was used in all the studies. The effectiveness of boron wash-out was evaluated by injecting boron solutions with different concentrations and also with different concentrations of wash-out reagents. The intensity of $^{11}B^+$ signal was monitored before and with the injection of wash-out solution for 120 sec. The effect of deposition of NaCl and CsCl from wash-out solution was investigated by sequential injection of synthetic mixture and NIST-SRM-951 boron solutions.

Results: Both NaCl and CsCl were found to be effective to wash out the boron from the ICPMS system, with CsCl showing much better performance in terms of signal to back-ground ratio. The use of CsCl showed much better stability of the boron ion current, when compared to the use of NaCl solution.

Conclusion: CsCl is an effective quick wash-out solution to minimize the memory effect in B-isotope ratio measurements with MC-ICPMS, using solutions with 20-50 ppb boron. This approach promises to circumvent the limitation of close matching of the boron concentration and the isotope ratio of the unknown sample with that of the reference material in SSB approach.

POSTER 2 - ISO: 9

Topics: Elemental analysis, Isotope ratio analysis, Environmental sciences

Keywords: strontium isotopic ratio, multielement analysis, geographic origin, asparagus, potatoes

Elemental composition and Sr isotopic ratio for authentication of primary agricultural products on the example of Asparagus from Bassano del Grappa and early potatoes in Southern Italy

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The interest of consumers in high quality food with a clear geographical identity has grown rapidly. Consumers have the right to make informed decisions about the food they purchase and have to be ensured that food products are protected for their provenance. Therefore, suitable analytical techniques are needed for determining the geographical origin of agroproducts.

The focal point of this research was to show how the elemental composition and $^{87}Sr/^{86}Sr$ isotope ratio fingerprint can be considered as promising tools for authentication both of “White Asparagus from Bassano del Grappa”, an Italian agricultural product covered by a Protected Designation of Origin (PDO) mark, and early potatoes in relation to different Italian geographic area of cultivation.

Our results show that especially the discrimination power of the Sr isotopic signature is the most promising parameter. White asparagus from Bassano del Grappa shows a distinct difference to literature values for the isotopic composition of Hungarian and Peruvian asparagus. A certain overlap can be observed with asparagus from Austria. A particularly important result is the high correlation between the Sr isotopic fraction in plant and the bioavailable fraction in soil, which can be used to distinguish agricultural products originating from different geographical areas. The same isotopic pattern is reflected in the agricultural products. A coefficient of variation (CV) was calculated to estimate the degree of similarity of mineral composition among geochemical profiles of soils and plants collected in the same production areas of Bassano del Grappa. For asparagus the elements characterized by a CV under 10% were 20 (among them Bi, Ti, Na, Zr, Tl). Ca, Fe, K, Mg, Mn, Na and P are able to discriminate between asparagus from Bassano del Grappa and asparagus from USA and Spain.

The authentication of the origin of early potatoes from three regions (Apulia, Sicily and Campania) in the south of Italy was studied by Zampella et al. (2008).The approach describes how the Sr isotopic signature and selected elemental concentrations ([Mn], [Cu], [Zn], [Rb], [Sr] and [Cd]) in potatoes were related to the geological substrates and the soil chemical properties influencing the bioavailability of elements in soils. In this work our attention is on the soil adhering to potatoes after collection in the field and size selection treatments. In this context, even gram amounts of soil adherent to the tubers may be compared to the soil collected in the respective fields for physical, mineralogical and geochemical patterns. In our case the soil adhering to potatoes has particle size distribution curves and XRD traces similar to the field soil, but higher amounts of smaller particles that make different the geochemical compositions.

The method used in this study has high operability and can be applied to other agricultural products, although it would be important to select adequate elements in addition to Sr isotope ratios.

POSTER 2 - ISO: 10

Topics: Isotope ratio analysis

Keywords: Nickel, Purification technique, Isotope ratio, MC-ICP-MS

Development of a rapid and quantitative nickel purification technique for accurate nickel isotopic analysis in geochemical reference materials

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Nickel (Ni) has five stable isotopes (58, 60, 61, 62 and 64) with abundance of 68%, 26%, 1.1%, 2.6% and 0.9%, respectively. Ni is a heavy metal and is released into the environment through anthropogenic activities. Therefore, understanding biogeochemical cycling of Ni in earth's surface is important to evaluate anthropogenic impact on ecosystems and human health. Recent developments of mass spectrometer allow detection of small isotopic variation of heavy elements in nature, and this technique has been applied to calculate quantitative mass balance budget of heavy elements. In case of Ni, the isotopic compositions of some geochemical samples were reported by Gueguen et al. (2013), Chernonozhkin et al. (2015), Gall et al. (2012) and Cameron et al. (2009 and 2014) and Hofman et al. (2014). In these previous studies, the resin containing dimethylglyoxime was used for Ni purification. This technique has several problems such as non-quantitative recovery of Ni, high Ni procedural blank values and time-consuming decomposition of the organic compound for isotopic analysis. In this research, we will report a new Ni purification technique using ion-exchange and chelating resins without dimethylglyoxime, and applied to Ni isotopic analysis of some geochemical reference materials.

Major elements of rocks are Na, Mg, Al, K, Ca, Ti, Mn and Fe. These elements must be removed by chemical purification prior to isotopic analysis to eliminate spectral interferences (58Ni; $^{58}Fe^{+}$, ^{60}Ni; $^{44}Ca^{16}O^{+}$, ^{61}Ni; $^{44}Ca^{17}O^{+}$, ^{62}Ni; $^{46}Ti^{16}O^{+}$) and non-spectral interferences affecting instrumental mass discrimination. Copper has to be also eliminated because Cu is doped for mass discrimination correction in this study. These elements were removed by three steps of solid phase extraction. First, Fe, Ti and Al were removed with a HF eluent by cation exchange chromatography. Second, alkaline, alkaline earth metals and Mn were separated with an ammonium acetate eluent using a chelating resin. Finally, Ni was separated from Cu with a HCl eluent by anion exchange chromatography. Recovery of Ni was 90-98% (JB-3) and 82-98% (BHVO-2) through this chemical procedure. In this presentation, we will report Ni isotopic composition of basaltic geochemical reference materials, JB-3 and BHVO-2.

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POSTER 2 - ISO: 11

Topics: Isotope ratio analysis

Keywords: mercury; MC-ICPMS; gas chromatography; speciation; isotope ratios; methylmercury

Development of a methodology for the accurate and precise measurement of compound-specific Hg isotopic composition in human and other biological samples by GC-MC-ICPMS.

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Methylmercury (MeHg) is a high neurotoxin which bio-accumulates in the living organisms causing bio-magnification in the trophic chain. Inorganic mercury (Hg(II)) is the much less toxic precursor of MeHg due to methylation by bacteria at the water sediment interface. It is clear that Hg mobility and bio-accumulation is extremely dependent on the species in which Hg is present in the environment. For example, in hair methylmercury is deposited directly from bloodstream while Hg(II) can be also adsorbed by the air from gaseous mercury. However, in spite of this evidence, only a few works reported the development of procedures for the simultaneous determination of the isotopic fractionation of different Hg species within the same environmental sample. Such methods can open a new dimension in the understanding of the Hg biogeochemical cycle, the study of the reactivity of chemical forms and to accomplish the study in interface biochemistry. So far there is no procedure developed for the accurate and precise measurement of compound-specific Hg isotopic composition in human samples. The aim of this work is the evaluation of the accuracy and precision obtained in the measurement of compound-specific mercury isotope ratios by GC-MC-ICPMS for its application in human samples.

The separation of both species was accomplished with a gas chromatograph coupled to a Neptune Plus Multicollector ICP-MS using a home-made transfer line. MeHg and Hg(II) were derivatized with sodium tetra (n-propyl) borate and extracted into hexane. The determination of the compound specific δ values was performed by a standard-sample-standard bracketing scheme using NIST 3133. Instrumental mass bias was corrected by the nebulization of a Tl standard solution continuously during the chromatographic run. Other parameters as the GC programme or the integration time in the measurement of isotope ratios have been evaluated.

The main difficulty of the compound-specific stable isotope analysis is the measurement of isotope ratios in transient signals. Therefore, this work is focused on the evaluation of the different instrumental parameters to obtain accurate and precise compound-specific Hg isotope ratios. Some of the optimized parameters include flow rates of the carrier and nebulization gases, chromatographic peak width, integration time, and data reduction strategies. The precision of the methodology is evaluated first with the delta zero standard NIST 3133. The determination of compound-specific δ values in the certified hair samples IAEA-085 and IAEA-086 and fish tissue SRM 1947 is also presented.

The methodology is evaluated for the measurement of compound-specific isotope ratios in transient signals by GC-MC-ICPMS in human and other biological samples. All the parameters were optimized to achieve the best precision and accuracy, and particular effort has been paid to the development of an efficient preconcentration step due to the low concentration of Hg species in the samples.

POSTER 2 - ISO: 12

Topics: Elemental analysis, Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: galena, Pb isotope ratio, Berezovskoe deposit

Chemical and Pb-isotopic zonality of galena (Berezovskoe deposit, Middle Urals): LA-Q-ICP-MS и HR-MC-ICP-MS data

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The Berezovskoe deposit (Middle Urals, Russia) comprises a unique gold-ore object with an extensive geological history. Its apparent zone structure implies the alteration of chemical and isotopic mineral composition. Massive deposit ore material sources can vary; this can be recorded in the zonality of large ore mineral crystals such as galena (Cannon et al., 1963, etc.).

The aim of the present work is to study the microelement and Pb-isotopic composition of a galena sample (approx. 2 cm) from a quartz-sulphide Berezovskoe deposit vein. It is grown on a beresite and thus represents the initial point of the growth of the individual crystal. The directional uniformity of the cleavage planes confirms the monocrystalline nature of the sample.

A NexION 300S Q-ICP-MS combined with a NWR 213 laser ablation system was used for microelement determination (energy – 10 J/cm^2, frequency – 10 Hz, spot diameter – 20 μm); a NIST 612 was used for calibration. Element concentrations were obtained for 9 points across the galena crystal (from the beresite border to the galena top). A Neptune Plus MC-ICP-MS was used for lead isotope ratio analysis of fragments (sub-mg) manually extracted from 3 zones of the galena sample (edge-centre-edge).

Fragments of galena were dissolved in nitric acid according to standard procedure. Sample preparations were tested directly and with primary lead chromatographic separation; no significant differences were observed. Average scatter values were 0.0066 for $^{208}Pb/^{204}Pb$ and 0.0017 for $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$; these did not exceed the determination error.

Microelement zonalities were established for a number of elements (ppm): Li 0 – 3.0, Mn 3.4 – 17.4, Cu 0.8 – 19.4, Zn 0 – 23.6, Ge 0 – 2.8, As 0 – 20.5, Se 0.4 – 13.9, Rh 52.5 – 132.2, Pd 33.1 – 89.1, Ag 5458.2 – 14446.1, Cd 1588.8 – 4013.2, In 1.5 – 4.2, Sn 59.3 – 213.3, Sb 2063.5 – 4974.6, Tl 21.1 – 40.4, Bi 7188.6 – 18955.6; Th and U concentrations were decreased (lower than 0.1 ppm). Various zonality types were observed for different elements: an increasing trend (Zn), a decreasing trend (Cu, Se), and, for the majority of elements, a bell-shaped distribution with maximum values grouped around the centre of the galena crystal. These zonalities apparently reflect the crystallization stages of ore minerals (tennantite-tetrahedrite series, sphalerite) and different material sources in ore-forming solutions.

Zones with high Mn, Rh, Pd, Ag, Cd, In, Sn and Bi concentrations were slightly enriched with ^{208}Pb and depleted in “uranium leads” (^{206}Pb, ^{207}Pb). This may indicate the involvement of an extra volume of crustal material into the ore-magmatic system during the growth of the galena crystal.

$^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios imply the existence of an ancient, probably precambrian crustal protolyte developed in a system with high m that was later subjected to metamorphic transformation in low crust conditions resulting in the loss of LILE with decreasing U/Pb and increasing Th/U.

POSTER 2 - ISO: 13

Topics: Isotope ratio analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: laser ablation, zircon, isotope ratio, uranium, lead

Application of ICP-MS Neptune Plus multi-collector and ICP-MS NexION 300s quadrupole spectrometers for LA-ICP-MS U-Pb dating of zircon: comparison and evaluation

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The main obstacle to the development of in-situ laser ablation (LA) U-Pb zircon dating methods using multi-collector mass spectrometers without a multi-ion counting (MIC) system is the non-simultaneous measurement of Pb, U, and Th isotopic signals. Hence, the required mass range for the realization of the U-Pb dating method is not achieved. The absence of a MIC system on multi-collector (MC) ICP-MS results in weak isotopic signals from the Faraday cups, especially from zircons with low concentrations of Pb, U, and Th.

This issue is successfully addressed using a quadrupole (Q) ICP-MS, which makes it possible to derive stable isotopic signals even from zircons having low concentrations of Pb, U, and Th. However, it should be noted that isotopic measurement error is higher when obtained by Q-ICP-MS as compared to the simultaneous isotopic signal collection from MC-ICP-MS.

Reference zircons 91500, Mud Tank and GJ-1 were analyzed both using a Neptune Plus (MC-ICP-MS) and NexION 300s (Q-ICP-MS) combined with an NWR 213 LA system (Nd:YAG, 213 nm).

A consequent measurement of isotopic signals in three lines was used for Neptune Plus: first line – Pb and Hg isotopes; second – ^{238}U; third – ^{232}Th (integration time – 0.066 s., idle time – 0.5 s).

The influence of laser ablation operation parameters on fractionation effect was examined, mass spectrometer measurement conditions were optimized, and a method for measuring Pb/Pb, Pb/U, and Pb/Th isotopic ratios followed by zircon age determination was developed.

In order to obtain a stable signal and to reduce the isotopic ratio measurement error using the Neptune Plus, the following optimized LA operation parameters were used: laser energy – 20-22 J/cm^2, frequency – 20 Hz, spot diameter – 50 μm (Mud Tank zircon with low Pb, U, and Th); energy – 11-13 J/cm^2, frequency – 10 Hz, 50 μm spot (91500 and GJ-1 zircons). The combination of NexION 300s and NWR 213 yielded in LA parameters of 11-13 J/cm^2, 10 Hz, 50 μm for Mud Tank zircon.

The concordant ages of reference zircons obtained under the optimized LA and MS operational conditions were as follows: 1054 ± 17 (MSWD = 1.05, 2% for 91500), 735 ± 12 (MSWD = 1.2, 2% for Mud Tank), and 606 ± 31 (MSWD = 0.38, 5% for GJ-1) using Neptune Plus; 1065 ± 7 (MSWD = 1.19, 0.7% for 91500), 719 ± 9 (MSWD = 0.91, 1.2% for Mud Tank), and 600.8 ± 4.4 (MSWD = 0.88 , 0.7% for GJ-1) using NexION 300s. All ages are in a good agreement with the published values.

Since the combination of NexION 300s and NWR 213 improved the accuracy and reduced the error of isotope ratio measurement for zircon U-Pb dating as compared to Neptune Plus, it was chosen for further zircon studies using LA-ICP-MS.

The study was carried out at the “Geoanalytic” Collective Use Centre. Financial support was provided by RSF grant No. 16-17-10283.

POSTER 2 - ISO: 14

Topics: Isotope ratio analysis

Keywords: radionuclide, iodine, ICP-QQQ, reaction cell

Analysis of radioactive iodine-129 by ICP-QQQ using MS/MS mode and a new octopole reaction cell with axial acceleration

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Since the explosion at the Fukushima Daiichi Nuclear Power Plant (FDNPP) resulting from the tsunami in 2011, determination of radionuclides in various samples has been of great interest. Especially important is the analysis of long-lived radionuclides such as iodine-129 (^{129}I: $T_{1/2}$ = 1.57 x 10^7 y) which are measured to investigate the diffusion of radionuclides from the FDNPP, and to study the mechanism of the explosion that occurred at the nuclear reactor.

In previous work[1)], an Agilent 8800 ICP-QQQ with oxygen (O_2) as the reaction cell gas was used to investigate the possible interference on ^{129}I from $^{127}IH_2$. The results indicated that both ^{127}ID and $^{127}IH_2$ are produced at a level that impacts significantly on the measurement of I at m/z = 129. Consequently, blank subtraction of total ^{127}ID and $^{127}IH_2$ needs to be applied to enable low-level determination of ^{129}I. There is also some evidence that, under some conditions, non-target ions can contribute to the signal at the target analyte mass, due to those non-target ions having lower velocity through the cell as a result of collisions with the O_2 cell gas. However, this effect is not yet thoroughly understood.

In the current work, we used a newly developed ICP-QQQ, the Agilent 8900, incorporating a new octopole reaction cell with axial acceleration function, which improves the transmission and therefore sensitivity of low-energy product ions. Axial acceleration also improves discrimination of slow-moving ions that can cause artifact signals and an apparent spectral interference at the target analyte mass, especially when a relatively heavy cell gas such as oxygen is used.

In this study, we used ICP-MS/MS with axial acceleration to study the effect of the IH_2 and ID interferences on radioactive iodide ^{129}I in more detail. Using ICP-QQQ with O_2 reaction cell gas mode and axial acceleration, we will present results showing a significant improvement in the measurable ratio of $^{129}I/^{127}I$ by in-cell energy discrimination with retarding axial field.

1) Y. Shikamori, K. Nakano, N. Sugiyama, M. Honda, A. Sakaguchi, K. Sueki, European Winter Conference on Plasma Spectrochemistry, Munster, Germany, Feb 23, 2015 FU2-PO06

ID: 168 / **POSTER 2 - ISO: 15**

Topics: Isotope ratio analysis

Keywords: geochemistry, Lithium, Boron, groundwater

Geochemical characteristics of hydrothermal fluids observed along Median Tectonic Line in Mie-Prefecture, Japan

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Precise measurement of isotope ratios of elements allows determining the origin of various geological materials. Mass-dependent isotopic variation of non-volatile elements can be now determined precisely through recent advances in inorganic mass spectrometry, in addition to conventional isotope ratios of volatile elements such as H, C, N, O, and S. In this study, we applied Li and B isotope ratios to hydrothermal fluids observed along Japan Median Tectonic Line (MTL) to understand their origin. MTL is the longest fault system in Japan related to subduction system in the plate tectonics theory, and the fluids along the fault may contain information from deeper part of the crust of ~30km in depth. The elements Li and B belong to light elements, and their isotopic variation in nature is very wide due to their large relative mass differences. The two elements are fluid mobile elements in fluid-rock interactions under high temperature, and are expected to keep the concentration and isotope information in later upwelling cooling stages. Their isotope ratios are therefore useful to detect hydrothermal fluids originated from deeper parts of the earth crust.

In this study, hydrothermal fluids from central Japan (Mie-Prefecture) were collected mainly as hot springs. Their 18O/16O and D/H ratios of H2O were determined by cavity ring-down spectroscopy. Values of d7Li and d11B were determined with ICP-MS with multiple-collector arrangement with reproducibility better than +/-0.03%. Sample amounts required for d7Li and d11B analyses were 10 ng and 50 ng under wet plasma condition.

Resultant 18O/16O-D/H ratios of water were mainly plotted along a fractionation trend of meteoric water and a mixing trend with seawater, but some samples have isotopic shifts toward heavy 18O/16O ratios, which indicate interactions with rocks under high temperature. Their d7Li and d11B ratios showed very low values for some samples, which suggest the fluids are originated from deeper part of the earth crust. In addition, a decoupling between the two isotope systems is observed. In the presentation, we will discuss the reason of the isotopic trend and decoupling including elemental concentration data.

POSTER 2 - ISO: 16

Topics: Environmental sciences

Keywords: River catchment, geology, Sr isotopes, elemental pattern, fish migration

Modelling elemental distributions and 87Sr/86Sr ratios in river water based on catchment geology: challenges and applications

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Freshwater river systems are an important part of the general hydrological cycle. They drain river catchments, transport the water in dynamic channels through the landscape towards the sea, are linked to groundwater resources and the associated landscape elements along the course of the river, and support a relatively high proportion of the global biodiversity (approximately 40% of global fish diversity and one quarter of global vertebrate diversity). However, freshwater systems have become the most endangered type of ecosystems world wide, with many catchments severely impacted by human activities. Therefore a comprehensive understanding of the state and dynamics in river catchments is needed for an improved future management.

The analysis the elemental and isotopic composition of river water and sediments has become an important tool for many management applications, e.g. the assessment of transport processes of water and sediments, erosion processes, weathering processes, the effect of human activities in catchments etc. As the chemical composition of river water is also reflected in different compartments of the biota associated with the riverine landscapes, also ecological questions can be targeted by studying the chemical composition of river water in relation to the chemical composition of the biota. Biota also often store and accumulate the chemical information in river systems, why they can be used as long-time indicators of the chemical history of river systems.

However, the basis for most applications is the understanding of the natural spatial and temporal distribution of elements and isotopes in the river water. Therefore increasingly maps of isotopic and elemental distributions in rivers and their associated sediments are created. As the major sources of elements and isotopes in river water are geology and weathering in catchments, overlaid by contributions of human activities, understanding the linkage between geology, weathering and the chemical composition of river forms an important step for an informed application of the chemical and isotopic composition for the different applications. Also potential temporal fluctuations oft he chemical composition and transport processes, e.g. during flood events, need to be considered.

Therefore this paper presents the experiences made during two case studies (Danube, from ist source down to ist mouth into to the Black Sea; Eg River in Mongolia) where the elemental and $^{87}Sr/^{86}Sr$ isotopic composition of river water was studied in relation to the geological composition of the associated catchments by ICP-MS methods. Exisiting models to describe the relation between catchment geology and river water composition are reviewed, and applied to describe these relations in the catchments of the River Danube and Eg River. Potential temporal effects related to changes in river discharge are described. Finally, the analytical challenges and potential applications are discussed in the light of the results.

POSTER 2 - ISO: 17

Topics: Sample introduction and sample preparation

Keywords: long lived radionuclides, incorporation, fast sample preparation

DETERMINATION OF 239PU, 240PU AND 241AM IN URINE BY MC-ICP-MS AFTER THEIR SIMULTANEOUS SEPARATION FROM THE MATRICE

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Monitoring of artificial nuclides in human excretion samples (e.g. urine) in context of the health impact is an important task for safety guards and radiation protection authorities. In particular, determination of ^{239}Pu and ^{240}Pu as well as ^{241}Am is of great interest because of their hazardous to the occupational or working personal after possible incorporation. Moreover, knowledge of ^{240}Pu/^{239}Pu ratio could be an excellent tool in order to reveal the origin of the release of these radionuclides. The most widely used analytical techniques for the determination of Pu isotopes in urine are radioanalytical techniques, such alpha-spectrometry or liquid scintillation radiometry. However, a long counting period, which can take from days to several weeks, depending on the sensitivity and precision required, could significantly restrict the usage of these techniques. In addition, radionuclide analysis of ^{239}Pu and ^{240}Pu by alpha spectrometry is very difficult, due to their similar alpha energies (5.24 and 5.25 MeV, respectively). Therefore, for accurate analysis of ^{239}Pu, ^{240}Pu as well as ^{241}Am in urine samples, mass spectrometric techniques have to be established.

Nowadays in the analytics exist several methods for the determination of Pu and Am in urine using mass spectrometric techniques. In spite of relatively simple measurements, these methods usually utilize labour- and time consuming sample preparation procedure, including chemical co-precipitation followed by selective separation of radionuclides by means of extraction chromatography. However, in the case of accident an availability of the method for the determination of ^{239}Pu, ^{240}Pu and ^{241}Am at mBq activity level in urine samples with the fast and simple sample preparation procedure would be absolutely preferable.

Therefore, the aim of the present study was to develop a rapid analytical method for determination of low activities (mBq/Sample) of ^{239}Pu, ^{240}Pu and ^{241}Am in urine. For the measurements a high sensitive multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) “Neptune/Plus” was applied. The samples preparation procedure was optimized. After the sample decomposition in a heating oven the Pu and Am were simultaneously separated from the matrix in one fraction, diluted with high purity water and directly subjected to the measurements. In order to receive the maximum separation yield, careful attention was payed to the different oxidation states of selected elements. This approach dramatically lowered the required analysis time and allowed to perform the determination of ^{239}Pu, ^{240}Pu and ^{241}Am in urine within about 4 hours after the sample income. In addition, usage of chemical was effectively reduced.

The developed method was validated on comparative measurements with the alpha-spectrometry as well as on the participating on interlaboratory comparisons. The results were corresponded with the expected values and will be discussed in detail in current poster.

POSTER 2 - ISO: 18

Topics: Isotope ratio analysis

Keywords: Plutonium, multiple ion counter inductively coupled plasma mass spectrometry (MIC-ICPMS), ion-counter calibration, polyatomic interferences

Procedures for precise isotopic analysis of trace Pu in environmental materials by multi-static MIC-ICPMS

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To further extend the analysis of Pu isotopes to trace and ultra-trace levels we use a ThermoNEPTUNE Plus equipped with a jet interface and 3 secondary electron multipliers (SEMs) and 2 compact discrete dynodes (CDDs). The ion counters (ICs) are positioned off-axis in an array that permits simultaneous collection of ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu. We present procedures for overcoming analytical challenges that may be encountered when conducting highly sensitive isotope measurements in this way. These include, (1) demonstration of an inter-measurement cross calibration technique to account for the difference in response between ICs. (2) A comparison of sample introduction systems has been performed to reduce memory effects and to circumstantially minimise the production of exotic interfering polyatomic species[1] such as $^{202}Hg^{40}Ar^{+}$. Repeat measurements have been performed on Pu reference material, CRM-126a (New Brunswick Laboratory), to test the reproducibility and accuracy of the proposed method. Finally, we evaluate the capability of this method to quantify Pu isotopes at the sub-1 fg g^{-1} level in environmental samples containing complex matrix components.

[1] Pointurier et al. (2016) *J. Anal. At. Spectrom.* **23**, 94-102

POSTER 2 - ISO: 19

Topics: Isotope ratio analysis

Keywords: Sr isotopes; origin determination; Laser Ablation

Systematic Assessment of the Potential of Elemental and Strontium Isotopic Signatures for Provenancing of Fruit Raw Products on the Example of Strawberries

Christine Opper, Sylvie Bonnet,Johanna Irrgeher, Konstantin Leonhartsberger, Caroline Aigner, Melanie Diesner, Thomas Prohaska

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The demand for methods capable for the determination of food origin and authenticity is constantly gaining public interest. Within this study, a method based on elemental and strontium isotopic analysis of strawberries was developed following prior established protocols. Strawberry raw products from 7 different countries were analysed for their elemental as well as Sr isotopic composition using ICP-MS.

The 87Sr/86Sr isotope ratios gave a clear differentiation between the investigated samples originating from different sites of growth. In combination with multielement pattern, an almost 100 % distinction was possible. No significant within-site heterogeneity was observed in either cases.

In addition, the influence of soil liming on the final Sr isotopic composition in the fruit was investigated in a controlled experiment. Additional influence parameters, such as the irrigation water and rainwater, were taken into account, as well. Although the 87Sr/86Sr isotope ratios of the lime, the irrigation water and the rain water were significantly lower than the isotope ratio of the soil (0.71609 ± 0.00071, U (k=2) – before liming and 0.71599 ± 0.00079 – after liming U (k=2)), the 87Sr/86Sr isotope ratios of the plants (0.71331 ± 0.00089, U (k=2)) and strawberries (0.71363 ± 0.00092, U (k=2)) showed a clear pattern: Sr isotope ratios in plant and fruits were shifted from the original signature before planting (0.70867 ± 0.00141, U (k=2)) towards that of the soil. Further, differences of the elemental pattern between limed and non-limed soil were insignificant.

These results confirm that the elemental and Sr isotopic information in the bioavailable fraction in soils is not altered by the investigated agricultural practices under the present conditions.

In a second step, we show first results of experiments on processed strawberries (e.g. storage of strawberries in yogurt) and the impact of the storing conditions on the elemental and Sr isotopic fingerprint. Laboratory experiments of strawberries processed to yoghurt showed that the original Sr isotopic fingerprint could be retrieved even in a small piece of strawberry extracted from the yoghurt after processing.

A contribution with similar content has been presented at RAFA (Recent Advances in Food Analysis) 2016, Prague, Czech Republic.

POSTER 2 - LA/LIBS: POSTER SESSION 2: Laser-assisted analysis

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com NORTH HALL

POSTER 2 - LA/LIBS: 1

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: Lithium Ion Battery, Laser Ablation, Imaging

Short-Circuit Determination by Spatially Resolved Analysis of the Quantitative Lithium Distribution on Cycled Lithium Ion Battery Electrodes via Laser Ablation - Inductively Coupled Plasma - Optical Emission Spectrometry (LA-ICP-OES)

Constantin Lürenbaum, Britta Vortmann-Westhoven, Martin Winter, Sascha Nowak

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Being successfully introduced into the market, lithium-ion batteries (LiBs) are already state-of-the-art for portable electronic devices and one of the most promising candidates for high capacity energy storage. Besides relatively high manufacturing costs and a long charging time, the major drawback is the degradation of the cell components, which is called aging and which minimizes both storage lifetime and cycle lifetime. Therefore, the focus of this work is the spatially resolved analysis of the lithium distribution on cycled anodes in self-assembled pouch bag cells.

Inductively coupled plasma - optical emission spectrometry (ICP-OES) coupled with laser ablation (LA) is an attractive combination of two methods for the spatially resolved investigation of lithium. Subsequently, the spatial lithium distribution was investigated by means of LA-ICP-OES. The spatial resolved analysis of lithium is important to confirm the assumption of dendrite growth, which leads to short-circuits, and to locate the region of lithium distribution on the anode, which affects the performance of LIBs.

POSTER 2 - LA/LIBS: 2

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: 3D, bioimaging, LA-ICP-MS, time-of-flight MS, image registration

Reconstruction of the 3D full elemental profile of Ceriodaphnia dubia using multimodal registration approaches

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The ability of lab-scale elemental probes to visualize the endogenous 3D distribution of major, minor and trace elements in an entire organism at a scale of <10 µm is still in its infancy. This work explores, in an application-oriented case study on Ceriodaphnia dubia, approaches to exploit the synergy within multimodal multiplexed data acquired by state-of-the-art lab-scale instrumentation with the aim of enhancing 3D elemental distribution profiling in small organisms. This work focuses on a combination of micro-X-ray computed tomography (µ-CT) and micro-X-ray fluorescence (µ-XRF) tomography and laser ablation - inductively coupled plasma - time-of-flight - mass spectrometry (LA-ICP-TOF-MS), as these techniques provide complementary information. A specimen of juvenile C. dubia, a small Daphniidae approximately 300 x 300 x 500 µm3 in size, was exposed to a mixture containing 25.2 µg Zn/L, 3.9 µg Ni/L, and 9.4 µg Cu/L. After exposure, a specimen was harvested, underwent fixation, staining, and embedding and was analysed using µ-CT and µ-XRF tomography. The voxel size of the µ-CT volume is 1.5 x 1.5 x 1.5 µm3, whilst the voxel size of the µ-XRF volume is approximately 30 x 30 x 30 µm3. The specimen was subsequently sectioned using a microtome, and every second 5 µm thick section was submitted to LA-ICP-TOF-MS analysis. The LA-ICP-TOF-MS data set consists of a set of 59 slices, spaced 10 µm apart in the z-axis, with a voxel size of approximately 5 x 5 x 10 µm3. External calibration was performed based on spiked gelatin droplets. 3D LA-ICP-MS data registration approaches reported in literature are based on the sequential registration of neighbouring slices (SSR), and operate under the assumption that shared features are present in neighbouring slices and that the relative position of these features can be extrapolated along the z-axis. This work describes and demonstrates a methodology to align a set of LA-ICP-TOF-MS 2D slices relative to the corresponding slices of the µ-CT and µ-XRF volumes with high accuracy. This correlative slice registration approach, abbreviated as CSR, permits the accurate reconstruction of the 3D LA-ICP-MS-based elemental distribution within specimens with a high level of inhomogeneity along the z-axis. The merits of CSR are highlighted by comparing the point cloud registered using CSR and the point cloud registered using SSR relative to the µ-CT data. Data fusion approaches are then applied on the multimodal data registered to improve the lateral resolution and decrease noise levels.

POSTER 2 - LA/LIBS: 3

Topics: Sample introduction and sample preparation, Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: laser ablation, icpTOF, imaging, stalagmite, carbonates

LA icpTOF – a reliable tool for rapid elemental imaging of carbonates

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With rapid increase of scientific interest in paleoclimate reconstructions in the past few decades, accurate dating of climate proxy archives has become quintessential for the development of solid, data-driven climate change models.

Among terrestrial climate archives, speleothems have the potential to offer the most reliable age models However, sampling uncertainty is a major issue and often the investigator faces the difficult task of compromising between spatial resolution and data quality. Moreover, areas with high detrital Th are not easily discernible by visual inspection, thus are difficult to be avoided while sampling and can induce larger uncertainties in the final age modelling.

In this contribution we present a new rapid screening technique for fast identification of sampling regions within speleothems that are less suitable for U-series chronology. High-resolution, rapid elemental imaging by means of LA icpTOF is implemented for the first time to resolve growth increments smaller than 40µm that show chemical fingerprints of detrital input (*e.g.*, high ^{232}Th and selected REE, low ^{238}U/^{232}Th ratio). In addition, coupling of the highly sensitive, simultaneous, and fast TOFWERK's icpTOF with the Teledyne CETAC's Aerosol Rapid Introduction System (ARIS) allows for much faster acquisition of data that can be further used in paleoclimate reconstructions. We compared key trace element concentrations of the ablated areas on a stalagmite collected from Izvorul Tăușoarelor Cave (Romania) with stable isotope data (δ^{18}O and δ^{13}C) previously acquired on the same growth bands and found concurrent geochemical trends.

Rapid imaging of stalagmites by means of LA icpTOF proves to be a powerful tool for dramatically decreasing the sampling uncertainty and increasing the accuracy and precision of the data used in paleoclimate reconstructions. Furthermore, the screening procedure is very fast, thus saving valuable analytical time and resources. The robustness of this method makes it easily adaptable to other types of samples that are relevant to paleoclimate studies (*e.g.*, corals, ice cores, etc.).

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICPMS, elemental fractionation, volatile element, ionization process, oxide melting point

Investigation of the cause of elemental fractionation in laser ablation-inductively coupled plasma mass spectrometry

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Introduction

Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) is a useful system for spot-elemental analysis of solid samples without any sample preparation (i.e., acid digestion). However, LA-ICPMS suffers from a technical issue, so called "elemental fractionation", in which elements in a sample show higher/lower amount than actual amounts, resulting in a poor accuracy of measurement. And, the effect of elemental fractionation depends on the properties of the elements. Elemental fractionation occurs during the processes of ①LA, ②particle transport from ablation cell to plasma and ③ionization in plasma [1]. In this research, we evaluated the effect of elemental fractionation in each process.

Experimental

In order to evaluate elemental fractionation, the trace elements in the glass standard material (NIST610) were measured in the following three-different ways; 10 mg of the powder of NIST 610 was digested in HF and HNO_3 at 180°C on a hotplate. Digested solution was subjected to ICPMS analysis. This samples was defined as a reference without elemental fractionation. Ablated particles of NIST610 were collected with a PTFE filter (pore size: 0.1 μm) and were digested as described above. Digested sample was analyzed by ICPMS. This data was represented by A with the effects of elemental fractionation derived form ①LA and ②particle transport. The ablated particles of NIST610 were also analyzed directly by ICPMS without any additional process. This data was represented by B with the effects of elemental fractionation during all processes (①+②+③). To maintain the plasma conditions constant, ablated particles and aerosols from ultrasonic nebulizer were merged in front of the ICP. Enrichment factors (EF) were calculated from the following equation (1)

$$EF_{A\ or\ B} = [(I_M/I_{Ba})_{A\ or\ B} / (I_M/I_{Ba})_{reference} - 1] \times 100\ (\%) \ldots \text{Eq. (1)}$$

"M" indicates elements and "I" indicates signal intensity obtained by ICPMS.

Results and Discussion

Elements with the oxide melting points lower and higher than that of the oxide of Ba were defined as group X and group Y, respectively. Group X showed negative EF_A, while EF_A was almost zero in Group Y. In addition, we confirmed that group X except As, Sb and Bi were not lost at the filtration step. It was previously shown that group X are tend to be enriched in small particles [2], suggesting that group X in small particles are lost during either or both processes of LA and particle transport. Also, group X that have higher volatility than Ba oxide showed positive EF_B, and group Y that have lower volatility than Ba oxide showed negative EF_B. This suggests that elemental fractionation effect depends on volatility of elements in particles. Furthermore, negative EF_A and positive EF_B in group X indicate that elemental fractionation in ③the ionization process is dominant.

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POSTER 2 - LA/LIBS: 5

Topics: Sample introduction and sample preparation, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: imaging, washout

Bloodhound technology from ESI: ultrafast signals

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Peak profile is becoming more important as the limits of elemental imaging by LA-ICP-MS are pushed further. Taller, narrower peak shapes are desired for their impact on sensitivity and experiment duration, image quality, and experiment speed: quicker pulses mean higher signal above background, higher spatial resolution, and the ability to scan the stages faster while achieving the same resolution.

Peak form is most commonly measured by peak washout (the time from the peak maximum to 1% of the maximum), but at the timescales current technology enables, peak width (1% to 1%, or sum of wash in and washout times) becomes a more valuable metric. An ability to provide predictable peak shapes is also important, but is more difficult to quantify. Peak widths are used here for discussion.

POSTER 2 - LA/LIBS: 6

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: laser ablation, feathers, metals, elemental distribution

Application of LA-ICP-MS in the search of elements pattern in feathers of Red-breasted flycatcher (Ficedula parva)

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The method of LA-ICP-MS was used in the study of bicolor (black and white) feathers coming from a red-breasted flycatcher *Ficedula parva*. The aim of the study was the analysis of: (1) the content of selected macro- and microelements in tested species' feather rachis according to their color, and (2) arranging the elements in a longitudinal section of feathers, i.e. from the peak of the quill to rachis. It was examined whether the rachis of feathers color difference is related to the distribution of elements such as Ca, Cu, Zn, widely considered essential in the synthesis of melanin. It was also checked whether the distribution of physiological elements (Ca, Co, Cu, Mg, Mn, Na, Zn) and toxic (Al, As, Ba, Cd, Ni, Pb, Sr) is dependent on the analyzed part of a feather. Aims of the study required development of analytical procedure ensuring rapid and sensitive determination of trace elements. Therefore, a series of experiments was conducted in relation to: (1) testing different strategies of calibration for quantifying elements in different parts of the feathers by LA-ICP-MS; (2) qualitative and quantitative visualization of the distribution and accumulation of elements in the longitudinal section of tested feathers.

The results obtained by LA-ICP-MS were comparable in terms of accuracy, precision and recovery results obtained after analysis by SN-ICP-MS (solution nebulisation ICP-MS). The developed analytical procedure was tested using certified reference material NCS ZC 81002b Human Hair (China National Analysis Center for Iron & Steel, China), and the quality of the ablation process has been verified using a scanning electron microscope (SEM-EDX). Data obtained from the analysis were processed statistically using standard statistical methods in combination with multivariate methods.

Results indicate that there is an association between the occurrence of elements, coloring and the area of the analyzed part of the feathers shaft. Statistically significant correlations were established between the color of the feathers shaft and the distribution of elements being involved in the synthesis of melanin (Ca, Zn). Our results indicate that further studies are warranted in larger.

POSTER 2 - LA/LIBS: 7

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Environmental sciences
Keywords: Food labelling, Rare Earth Elements, Laser Ablation ICP-MS

Assuring the geographical origin of food products by labelling with rare earth elements and detection using solution based and laser ablation ICP-MS

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The demand for methods for the determination of the geographical origin of food and agricultural products has increased over the last years due to growing demand for regional products, and in view of recent food scandals. Food products which have a direct relationship to the local soil, either through absorption from the soil in the case of plants or by feed intake in the case of animals, reflect the regional distribution of trace elements and their provenance can therefore be established by means of trace element fingerprinting. However, this approach is not generally applicable for products of conventional agriculture, as animals are usually fed with compound feeds of different origin, and vegetables are grown on substrates in glasshouses. Such products can be labelled artificially by adding trace elements to the substrate for plants or the feed for animals. Rare earth elements (REE) are ideally suited for this purpose due to their low toxicity and low natural background levels. Therefore labelling can be achieved using very small quantities of REE, provided that sensitive techniques such as ICP-MS are applied for analysis.

In this contribution we present a study on the labelling of food products of both plant and animal origin, namely tomatoes and eggs, using REE. In case of tomatoes, Neodymium and Erbium were added either to the substrate or to the irrigation water, both leading to distinct enrichment relative to natural values. Eggs were labelled by spiking compound feed for hens with Terbium and Thulium, also resulting in considerably increased contents. Samples were analysed using solution based ICP-MS after digestion using a high pressure asher (HPA-S, Anton Paar). Laser ablation ICP-MS (LA-ICP-MS) was used as an alternative method, allowing REE detection in diverse food matrices with little or no sample preparation. The application of LA-ICP-MS is facilitated by the fact that the present application requires only detection of relative enrichment of the REE used for labelling. Absolute quantification is not necessary, eliminating the needs for matrix-matched standards crucial for many LA-ICP-MS applications. However, the abundances of REE in some samples such as eggshells are very low even after labelling, posing a challenge for LA-ICP-MS. Sufficiently high sensitivity could be achieved using an Agilent 8800 triple quadrupole ICP-MS equipped with an s-lens, a set of ion lenses typically used in semiconductor industry, and a second foreline pump enhancing ion transport efficiency due to lower interface pressure.

POSTER 2 - LA/LIBS: 8

Topics: Sample introduction and sample preparation, Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Nanomaterials, Environmental sciences, Plasma source fundamentals, instrumentation and mechanisms
Keywords: Laser ablation, nanoparticles

Benefits of Fast Data Acquisition with Laser Ablation and Quadrupole ICP-MS

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Recent advances in quadrupole ICP-MS have led to the ability to acquire data at much shorter dwell times than those needed for routine quantitative sample analysis (typically 25-100 ms). These short dwell times of 10-100 µs have meant that transient particles and their resulting ion plumes can be tracked as they exit the plasma and arrive at the detector. This leads to a ‘rise and fall‘ response which can be quantified to allow the characterisation of nanoparticle suspensions and slurries. Work across a number of application areas has taken place and single particle ICP-MS is becoming more and more prevalent in laboratories across the globe.

Characterising particles arriving as part of a liquid aerosol is one approach but this poster presents data obtained using a nanoparticle application module and a 193 nm laser ablation system. This system allows fundamental studies on the ablated material and sample homogeneity. Profiling a single ablation pulse on a quad instrument may have applications in several fields. We will present the systems used, details on the software adaptations and results from our studies.

POSTER 2 - LA/LIBS: 9

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LIBS, linear discriminant analysis, multivariate statistics, corn, maize

Qualitative discrimination analysis of corn hybrids by laser-induced breakdown spectroscopy

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The analysis of biological samples is a relatively new field of applications for laser-induced breakdown spectroscopy (LIBS). Within this field, LIBS is generally used to study the spatial distribution of elements (or nanoparticles) in the samples or to identify/discriminate biological sample types (e.g. tissues, bacteria, bioaerosols, etc.). The present investigation falls in the second category, as our research goal was to assess the discrimination capability of multivariate statistical data evaluation of LIBS spectra in the case of corn (maize) hybrid plant samples (seeds). This analytical application promises important benefits for the agricultural/food chemistry practice, where the objective identification of plant species is required for commercial and regulatory purposes. This is so because although the identification of plant species can generally be done via visual observation performed by an expert, but in cases of closely related species (e.g. hybrids), and/or when only a part of the plant (e.g. the seed) is available for testing, the objective identification is only possible by instrumental chemical analysis. Presently, such analyses are performed in laboratories, using tedious extraction procedures followed by electrophoretic or mass spectroscopy measurements. At the same time, LIBS was already shown to be capable of providing fast, largely sample presentation free and powerful qualitative discrimination analysis for other sample types by using compact instrumentation in the field.

In this study, we had two sample sets composed of seeds from corn hybrids. One set contained seeds from hybrids grown on very similar soils and under comparable conditions (Set A), whereas the other set contained seeds from one hybrid cultivated on seven different soils (Set B). We cleaned the seeds from external contaminations and acquired the LIBS spectra from both the pericarp and the endosperm parts, by employing a compact, portable LIBS system (LIBScan 25+, Applied Photonics, UK). The spectral data was then analyzed by using the combination of various normalization and multivariate statistical methods (e.g. PCA, LDA and k-means clustering).

Linear discrimination analysis was found to provide the best performance out of the tested methods; within Set A the accuracy of the discrimination was as good as 70-85%. Variation in the soil composition clearly makes the discrimination more difficult, as the accuracy for Set B was significantly lower (60-70%).

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: silicon carbide, laser ablation in liquid, isotope dilution analysis, nano particles, ICPMS

Quantification of trace elements in sintered silicon carbide by inductively coupled plasma-mass spectrometry with laser ablation in liquid and isotope-dilution analysis

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Introduction

Silicon carbide (SiC) has unique physical and chemical properties, such as chemical resistance, high thermal conductivity, high dielectric breakdown field strength and wide bandgap, and has been widely used for a variety of industrial applications (i.e., semiconductors, grinding materials and nuclear reactors) [1]. Because those properties of SiC are affected by the contamination of trace impurities [2], it is necessary to determine impurity levels in SiC materials. However, it is difficult to decompose SiC by acid digestion. In this research, we focus on laser ablation in liquid (LAL) sampling. LAL sampling has been used to generate sub-micro- or nano-sized particles from solid materials with less contamination compared with using a crusher [3]. We tried to analyze trace impurities in sintered SiC by means of LAL-inductively coupled plasma-mass spectrometry (ICPMS). Furthermore, to improve the precision of quantification, we used isotope dilution (ID) analysis for LAL-ICPMS.

Experimental

A sampling camber made of PFA was used for LAL sampling. Sintered SiC was placed in the sampling chamber, and 5.6 mL of ultrapure water was added. The sample surface was irradiated through the water. The obtained particles were collected into a PFA vial and digested in HNO_3, HF and H_2SO_4 using a microwave oven (1 h). After digestion, the solution was transferred to a platinum crucible, heated on a hot plate (350°C) to remove H_2SO_4, and diluted with 0.1 M HNO_3. The diluted solutions were analyzed by ICPMS. In the analysis using LAL-ID-ICPMS, ^{49}Ti-enriched solution was added to the solution containing LAL-sampling particles, followed by digestion and analysis using ICPMS as described above. In addition, the LAL-sampling particles were subjected to the analyses using laser-Raman microscope and dynamic light scattering photometers to investigate changes in chemical composition and the distribution of particle size, respectively.

Results and Discussion

Nano particles (average of particle diameter = 259 nm) were generated from the sintered SiC by LAL sampling. In addition, laser-Raman microscopy revealed that sintered SiC was transformed from hard-to-digest forms to acid digestible forms, which were composed of silicon and amorphous carbon, suggesting that the transformation occurred by the melting-congelation process during LA. Indeed, it was confirmed that obtained particles were completely decomposed by acid digestion in a microwave oven only for an hour. Taken together, we concluded that generation of nano particles and transformation of chemical composition by LAL allow us to digest SiC effectively. Now we are trying to determine impurity levels by LAL-ICPMS and also to improve the precision of quantification by LAL-ID-ICPMS.

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POSTER 2 - LA/LIBS: 11

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution
Keywords: LA-ICP-MS, calibration, hydrocolloid gels, gelatine

Hydrocolloid gels and chelating media disks as calibration standards in LA-ICP-MS imaging

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Calibration in laser ablation ICP-MS imaging is challenging due to the absence of suitable microanalytical certified reference materials that are composed of biological materials, especially posing quantification problems for imaging in disciplines such as biology, biomedicine, plant physiology, etc. So far pressed pellets of certified reference materials, spiked gelatine gels, spiked polymeric films[1-3], etc. have been used for calibration purposes. Nevertheless, homogeneity of these custom made materials is always doubtfull and sometimes lacking. In this work several calibration standards based on different materials and preparation procedures were rigorously tested for homogeneity.

Gelatine gels, spiked with (multi)element solutions have by now been extensively used as calibration standards in LA-ICP-MS analysis and (bio)imaging. Either in their native (wet) form or after drying they seem very appealing as they are supposed to mimick protein matrices, and are used as quasi matrix-matched calibration standards in e.g. brain or other protein tissues LA-ICP-MS (bio)imaging work. For plant physiological imaging work polysaccharide hydrocolloid gels as calibration standards have not found much use, except maybe agarose gels, although a wide range of hydrogel forming polysaccharides exists, such as e.g. methylcellulose, xanthan gum, carrageenan, alginate, guar gum and gellan. Other still unexplored materials with great potential are chelating media, such as for instance 3M Empore™ disks based on selective functional groups (iminodiacetate functionalized SDB cross-linked polymer). All these materials have the potential to be used as matrix-matched element standards in various fields and as such have been tested in this work for microanalytical calibration, i.e. based on pixel sizes associated with beam sizes as low as 5 m.

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POSTER 2 - LA/LIBS: 12

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution

Keywords: LAMS, Kinetic energy distribution, Ion funnel, Retarding Field Energy Analyzers

Investigation of the kinetic energy distribution generated with a Laser Ablation-Ion Funnel (LAFU) source

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In comparison to LA-ICPMS, laser ablation mass spectrometry (LAMS) can offer various advantages for the analysis of solids, including high ionization efficiency, low running costs, and the absence of interferences originating from the ICP. Unfortunately severe limitations occur, which have affected the implementation of this method in elemental and isotope analysis. When a pulsed, high-power laser beam is focused onto the surface of a target a portion of the illuminated mass is ejected end ionized. The produced ions present a broad kinetic energy distribution which, among other variables, makes their exploitation for direct mass analysis a challenge, since electrostatic focusing devices are effective in high vacuum and for ions with a very narrow kinetic energy distribution. In this work we aim to investigate the influence of a novel laser ablation ion funnel (LAFU) ion source on the kinetic energies of the ion cloud produced by a high intensity laser pulse. The LAFU ion source consists of an Rf-only ion funnel in combination with a convergent divergent (CD) nozzle. The ions are formed in a region of elevated pressure upstream the nozzle and further cooled and confined using a repulsive quasi-stationary potential wall created with a combination of Radiofrequency (RF) applied to a series of stacked ring electrodes with decreasing diameter towards the mass spectrometer orifice[1,2]. The convergent-divergent supersonic (CD) nozzle before the ion funnel creates the necessary acceleration to transport the ions through the funnel without the need of a DC gradient. An in house made retarding field energy analyzer was built for the analysis of the kinetic energy distribution.[3]

This presentation will discuss the effects of collision gas pressure and flow rate as well as the Rf-frequency and amplitude on the ion kinetic energies of various elements downstream the ion funnel.

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POSTER 2 - LA/LIBS: 13

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Plasma source fundamentals, instrumentation and mechanisms

Keywords: LIBS-stratigraphy, galvanic coatings, ablation rate, plasma shielding, light-plasma-interaction, depth-profiling

Depth Profiling of Galvanoaluminium-Nickel Coatings on Steel by UV- and VIS-LIBS: Hints to wavelength-dependent plasma coupling influencing the effective ablation rate

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Laser induced depth profiling[1,2] was applied to the investigation of galvanised steel sheets as a typical modern multi-layer coating system for environmental corrosion protection. The samples were ablated stepwise by the use of two different wavelengths of a frequency-converted Nd:YAG-laser, 266 nm and 532 nm, with a pulse duration of τ = 4-10 ns at fluences ranging from F = 50 - 250 J/cm^2.

The emission light of the resulting plasma was analysed as a function of both penetration depth and elemental spectrum in terms of linear correlation analysis[3]. Elemental depth profiles were calculated and compared to EDX-cross sections of the cut sample.

A proven mathematical algorithm designed for the reconstruction of layer structures from distorted emission traces, caused by the Gaussian ablation profile[2,4] can even resolve thin intermediate layers in terms of depth and thickness. The obtained results were compared to a purely thermally controlled ablation model.

Thereby light-plasma coupling is suggested to cause deviations in the ablation behaviour of Al but not of Ni. The average ablation rate (AAR) as a function of fluence F for Ni ranges from 1 - 3.5 µm/pulse for λ = 266 nm as well as for λ = 532 nm. In contrast, the AAR range for Al differs from 2 - 4 µm/pulse for λ = 266 nm and 4 - 8 µm/pulse for λ = 532 nm in the exact same fluence range on the exact same sample.

This points towards an element-selective wavelength-dependent plasma shielding[5] which influences the metal ablation with pulsed ns-lasers in addition to thermal heat transfer in the bulk metal.

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POSTER 2 - LA/LIBS: 14

Topics: Elemental analysis

Keywords: conducting polymer, ashing, ICP-MS, LIBS

Analysis of SiO2-enforced conducting polymer using ICP-MS and LIBS

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Since conducting polymers are consisted of long chains, repeating themselves with free electrons and formed electromagnetic shielding of electronic circuit, they can be used as antistatic coating materials. Their important application field is expanding into electroluminescent displays, such as OLED, as a hole injecting electrode owing to the conductivity that affected by the presence of doped materials. Nowadays, the doped metals and/or materials for practical usage became complicate and important because they determine physical and electrical properties, so that their analysis and characterization became more important and difficult for production process and quality control.

In this work, we developed characterization and analytical method of SiO_2-enforced conducting polymer containing ZnO. First, we used FT-IR, EDX and XRF for component analysis, determining base material and additives and then studied a pre-treatment process based on microwave digestion and ashing followed by acid digestion. For optimized condition, samples in a quartz crucible were heated up to 800 ℃ and then dissolved by concentrated HF and HNO_3 solutions for ICP-MS measurement. The determined concentration of Zn was near 0.5%, obtained by standard addition with In as an internal standard. Based on the determined information of major components and additives, elemental mapping, characterization, and component validation were carried out using laser-induced breakdown spectroscopy (LIBS) and laser ablation ICP-MS (LA-ICP-MS). Conclusively, this newly developed analytical method show good agreement with LA-ICP-MS and LIBS that presented excellent potential for direct analysis and characterization of conducting polymers for production control.

POSTER 2 - NANO: POSTER SESSION 2: Nanomaterial characterisation and analysis

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com NORTH HALL

POSTER 2 - NANO: 1

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials
Keywords: silver nanoparticles, clay additives, AF4, ICP-MS, size characterization

Use of ultrafiltration and AF4-ICP-MS for the study of silver released from silver nanoparticles-based clay additives used in animal feeding

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It is well known the uses of both metallic silver and silver salts in many aspects of medical industries due to their antimicrobial properties, with a minimal risk of toxicity in humans. Their use in animal feeding as prebiotics have remain minimised, mostly because of the low cost antibiotics used as growth promoters. However, after the ban of this practice in the European Community, silver compounds appear as a potential alternative. Clays are commonly used in animal feeding for different technological, nutritional or environmental applications. In this work, two different clays, sepiolite and kaolin, have been used as vectors for silver nanoparticles oral administration.

On the basis for a better understanding on the response on metabolism and effects over the digestive microbial ecosystem of the animals treated with silver nanoparticles, a study of the transformations of silver under digestion conditions is proposed. As first approach, the behaviour of these materials in ultrapure water, HCl 0.01 M and in vitro digestibility assays media (corresponding to a three-step enzymatic incubation) has been studied. Total amount of silver released and percentage of ionic silver (ultrafiltrated through a 3 kDa pore size membrane) have been determined by ICP-MS. The rest of silver forms released have been characterized by Asymmetric Flow Field-Flow Fractionation (AF4) coupled to ICP-MS as detector. Dynamic light scattering (DLS) and electronic microscopy techniques (FESEM) have been used to compare the results obtained.

Differences on the total amount of silver released and percentage of ionic silver have been observed when comparing the two materials studied under the different conditions tested. The use of AF4 coupled to ICP-MS allows to differentiate silver forms released respect to those clay particles remaining in solution, although the use of different techniques, combined with prefractionation methodologies on leachates in different media is required to understand the processes undergone by silver under ingestion conditions.

This work was supported by the Spanish Ministry of Economy and Competitiveness and the European Regional Development Fund, project CTQ2015-68094-C2-1-R (MINECO/FEDER).

POSTER 2 - NANO: 2

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials
Keywords: Nanoparticles, nanomaterials, hydrodynamic chromatography, ICP-MS

Reconsidering hydrodynamic chromatography coupled to ICP-MS for the analysis of nanomaterials

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Engineered nanoparticles (ENP) are increasingly being incorporated into consumer products and reaching the environment at a growing rate. This fact requires the adaptation of existing techniques and methods, or the development of new ones to monitor their ocurrence, fate and transformations. In order to understand the environmental impact of ENP, it is critical to discriminate among dissolved and particulate forms. Different techniques and methodological approaches for the characterization and quantification of ENP and its derivatives in complex samples have been recently reviewed [1].

Asymmetric flow field flow fractionation (AF4) and hydrodynamic chromatography (HDC) are commonly coupled to ICP-MS as element specific detector for the separation and determination of inorganic ENP in a variety of samples. Although HDC is a robust and versatile separation technique, its resolving power is much lower than AF4. However, separations take place in a shorter time and dissolved low molecular mass species are not lost, as in AF4 due to the ultrafiltration membranes used in its separation channel. Thus HDC-ICP-MS can provide simultaneous information about dissolved and particulate species of an element in less than about ten minutes, which is not the case for AF4.

Most applications of HDC-ICP-MS involve the use of the commercialy available PL-PSDA HDC column and a proprietary mobile phase, comprised of a salt mixture and surfactants. In this work, chromatographic parameters as well as mobile phase compositions have been systematically studied with the column cited above, to evaluate the perfomance of HDC-ICP-MS for the simultaneous determination of dissolved species and nanoparticles of the same element. Special attention was paid to the resolution achieved between dissolved species and nanoparticles and their column recovery.

This work was supported by the Spanish Ministry of Economy and Competitiveness and the European Regional Development Fund, project CTQ2015-68094-C2-1-R (MINECO/FEDER).

[1]F. Laborda, E. Bolea, G. Cepriá, M. T. Gómez, M. S. Jiménez, J. Pérez-Arantegui, J. R. Castillo, Analytica Chimica Acta, 2016, 904, 10-32

POSTER 2 - NANO: 3

Topics: Nanomaterials

Keywords: nanoparticle, spICP-MS, single particle, microsecond dwell time

Analysis of gold and silver nanoparticles and their aggregates by means of spICP-MS using millisecond and microsecond dwell times

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As the number of nanoparticle applications in technology, medicine, and consumer products increases, there is also a growing interest in the characterization of nanoparticles, engineered as well as natural occurring. Common used inorganic particles are gold and silver (AuNP and AgNP), which can be found in biosensor applications, cancer treatment, or disinfection.[1] To optimize those applications and deal with risk assessments, the particles' most important characteristics like number concentration, particle size distribution, and elemental composition need to be determined – at best by a fast and versatile method.

Most rapid techniques for particle characterization lack a specific look at the single particle itself – such as UV/vis-spectroscopy using unique properties of some nanoparticles like AuNP's light absorption. Unfortunately, these methods can only analyze the whole ensemble of particles, whereas microscopic techniques such as transmission electron microscopy (TEM) or atomic force microscopy (AFM) can determine properties of single particles with impressive spatial resolution. However, they call for time consuming sample preparation and sophisticated data evaluation. A technique providing fast, robust, and reliable information on the entirety of all particles as well as the individual particle is the single particle inductively coupled plasma-mass spectrometry (spICP-MS).[2,3]

Using the spICP-MS-Method with a quadrupole-based mass spectrometer (PlasmaQuant MS Elite, Analytik Jena, DE) thousands of nanoparticles can be characterized for their number concentration, size distribution, and elemental composition in a short period of time with simple sample preparation. Additionally, shortest dwell times in the range of microseconds can provide information on the shape and size of gold and silver nanoparticle aggregates by resolving the cloud of ions generated in the plasma. This study compares the characterization of nanoparticles by millisecond and microsecond dwell times. The nanoparticles are made of gold and silver with diameters ranging from 10 to 80 nm. The applicability of different dwell times was tested by analyzing separate particles as well as aggregates of those.

[1] Dreaden, E. C.; Alkilany, A. M.; Huang, X.; Murphy, C. J.; El-Sayed, M. A. Chem. Soc. Rev. 2012, 41 (7), 2740.

[2] Degueldre, C.; Favarger, P.-Y.; Wold, S. Anal. Chim. Acta 2006, 555 (2), 263.

[3] Abad-Álvaro, I.; Peña-Vázquez, E.; Bolea, E.; Bermejo-Barrera, P.; Castillo, J. R.; Laborda, F. Anal. Bioanal. Chem. 2016, 408 (19), 5089.

POSTER 2 - NANO: 4

Topics: Elemental analysis, Nanomaterials

Keywords: spICP-MS, nanoparticles, nanoparticle characterization

Characterization of oxide nanoparticles surface-modified by metals using Single Particle Inductively Coupled Plasma Mass Spectrometry

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In the last decades, nanotechnology has become one of the most significant and innovative fields of material science. The application of nanoparticles (NPs) and nanocomposites in catalysis is particularly desirable due to their specific capabilities. The attributes of NPs (size distribution, composition, structure, etc.) can greatly influence their catalytic perfomance in terms of selectivity, activity or lifetime, therefore the thorough characterization of NPs is essential. One of the promising, novel nanoparticle characterization methods is Single Particle Inductively Coupled Plasma Mass Spectrometry (spICP-MS), which shows distinct advantages over other established NP characterization methods, especially for aqueous NP dispersions. The potential of spICP-MS has already been demonstrated for some metallic NPs in some environmental, biological and food chemistry applications.

The aim of the present study was to assess the analytical performance of spICP-MS in a special application: the characterization of oxide nanoparticles surface-modifed by the attachment of small metallic nanoparticles. Several metal/oxide nanocomposites (e.g. Pt on SiO_2, ZnO, etc) synthesized for catalytic purposes were investigated. One of the challenges of this analytical task is that the NPs anchored to the surface of the carrier particles have a much smaller size (< 5 nm diameter) than the current size detection limits of spICP-MS. In this study, spICP-MS was also tested as a tool to selectively determine the concentration of the metal on the surface (wt%), which is also important in catalytic applications. A detailed comparison and discussion is given of the performance of the method with reference to that of transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy-scanning electron microscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS) and solution mode ICP-MS. The effect of instrumental parameters on the NP signal and the accuracy of the results were also studied. It was concluded that spICP-MS is not only the most practical and fastest analytical method, but also one that provides the most reliable results in this application.

POSTER 2 - NANO: 5

Topics: Nanomaterials

Keywords: Graphene oxide, biodistribution, ICP-MS

Determination of Graphene Oxide Nanosheets in Biological Tissues Using Post-Administration Labeling with Oligonucleotide-Conjugated Gold Nanoparticles

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Graphene oxide nanosheets (GONs) have been considered as potential candidates for drug delivery and cancer therapy owning to their excellent aqueous processability, amphiphilicity, and surface functionalizability. However, to study the biodistribution of carbon-based nanomaterials (NMs) remains a technical barrier since conventional methods relying on conjugating radioisotopes or fluorescent probes onto these carbon-based NMs would change their original surface properties and suffer the risk of tag detachment following administration. To overcome these limitations, we employed the oligonucleotide-conjugated gold nanoparticles (AuNPs) to label these administrated GONs in digested organs/tissues for their quantification through indirect measurement of signals of gold by ICP-MS. To optimize the labelling of GONs using oligonucleotide-conjugation AuNPs, the effect of the oligonucleotides ($A_{20}R_{20}$, $A_{20}R_{40}$, and $A_{20}R_{60}$, R: random sequence including A, T, C, G) as well as the incubation pH, time, and concentration were evaluated. Besides, an online sample pretreatment scheme utilizing a homemade minicolumn packed with C_{18} resins was optimized as well for efficiently separating these $A_{20}R_X$-AuNP-labelled GONs and these residual $A_{20}R_X$-AuNPs. After overall method's optimization, it was found that the $A_{20}R_{20}$-AuNPs have the strongest binding affinity to label these administrated GONs in biological tissues with the equilibrium dissociation constant (K_d) of 36.0, 52.6, and 99.0 fM for 70-nm, 140-nm, and 220-nm GONs, respectively, and the detection limits can reach 10.5 ag L^{-1} (70-nm GONs), 10.5 ag L^{-1} (140-nm GONs), and 30.4 ag L^{-1} (220-nm GONs), respectively. Moreover, the biodistribution of intravenously administrated 70-nm, 140-nm and 220-nm GONs 10 min and 12 h post injection will be performed to demonstrate the applicability of our proposed method.

POSTER 2 - NANO: 6

Topics: Nanomaterials, Environmental sciences

Keywords: Nanoparticle, sp-ICP-MS, Environment

Fate of nanoparticles in environmental matrix: Dissolution Study

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Human and environmental exposure to engineered nanomaterials (ENM), extensively used in several applications ranging from healthcare to coatings and paints, has led to concerns regarding their risk. In order to predict the environmental behavior of ENM, become important to deeply study the interaction between ENM and the environmental matrix. Parameters like pH, Ionic strength, Organic Matter (OM) and Solid Particulate Matter (SPM) affect dynamic properties such as Aggregation/Agglomeration, Dissolution, and Surface Chemistry. The aim of this study is to evaluate the dissolutions rate of CuO and Ag nanoparticles by changing different parameters(i.e. pH, OM, SPM). The approach presented here can greatly support further investigation focused on homo-heteroagglomeration of nanoparticles in environmental matrix. The principal technique used to perform this tasks is single-particle Inductively Coupled Plasma-Mass Spectrometry (sp-ICP-MS), that can give, at the same time, information related to particle size-distribution and dissolved ions.

POSTER 2 - NANO: 7

Topics: Nanomaterials, Environmental sciences

Keywords: Silver nanoparticles, Soils, Adsorption studies, Leaching tests, SP-ICP-MS

Interaction studies of silver nanoparticles with soils using inductively coupled plasma techniques

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The production and use of silver nanoparticles (AgNPs) has extremely increased during last years due to their antibacterial and unique physicochemical properties. As a consequence of the spread of their manufacturing, these particles are released inevitably into the environment being soils the main sink of disposal. Once in the soil, AgNPs can be adsorbed/desorbed from solid components affecting their mobility, transport and bioavailability.

To understand adsorption processes in soils, lab-controlled kinetic studies were performed. With this purpose, soils with different physicochemical properties and AgNPs with distinct sizes and coatings were tested. These experiments consist on putting in contact 0.5 g of soil with 20 mL of a solution containing AgNPs. The silver content in the supernatant solution was determined with inductively coupled plasma optic emission spectrometry (ICP-OES) at a specific time.

Twenty-one days after batch adsorption studies, soils were submitted to leaching procedures. To perform these tests, 0.5 g of soil was rotated with 5 mL of extracting agent solution: deionized water (DIN) or diethylenetriaminepentaacetic acid (DTPA). To assess the mobility and bioavailability of AgNPs and to determine if their form is maintained during adsorption/desorption processes, leachates were analysed with ICP-OES and single particle inductively coupled plasma mass spectrometry (SP-ICP-MS).

The batch adsorption tests performed using soils with different physicochemical properties showed that cation exchange capacity and loss on ignition are the main parameters controlling the Ag kinetic adsorption process. On the other hand, the adsorption kinetics of highly negative charged citrate coated AgNPs is slower than neutral polyethylene glycol AgNPs (PEG-AgNPs) and negative charged polyvinylpylorridone AgNPs. Furthermore, the adsorption of AgNPs with different sizes was also tested and it was determined that small citrate AgNPs (40 nm) were slightly less retained than 200 nm citrate AgNPs. This could be due to the fact that more particles were present in the 40 nm solution than in the 200 nm AgNPs solution, working at the same silver concentration.

The DIN leaching tests indicated that AgNPs were strongly retained to soils. However, according to SP-ICP-MS analyses, the small silver fraction recovered from soils maintained their nanoform, except for 100 nm PEG-AgNPs and 40 nm citrate AgNPs. For DTPA leaching tests the amount of silver in the extracting solution was higher, but there was no presence of AgNPs in none of the leachates.

In conclusion, AgNPs were quickly and strongly adsorbed onto soil surfaces, despite the fact this process varies depending on NPs physicochemical properties and soil characteristics. Leaching tests showed low mobility and bioavailability of these particles. The analysis of DIN leachates indicated that AgNPs maintain their form after being desorbed.

POSTER 2 - NANO: 8

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials, Environmental sciences
Keywords: CE-SP-ICP-MS, nanoparticles, separation, surface coating

IMPLEMENTATION OF CE-SP-ICP-MS FOR SEPARATION OF SILVER NANOPARTICLES WITH DIFFERENT SURFACE COATINGS

Darya Mozhayeva, Carsten Engelhard
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The stability of nanoparticles (NPs) in aqueous solutions is highly dependent on the chemical composition and the structure of the NPs surface coating. The coating prevents NPs from aggregation, therefore increasing the lifetime of NPs in consumer products and the environment. The surface coatings can also change the charge of the NPs, which influences their bioavailability.

CE-SP-ICP-MS (capillary electrophoresis – single particle – inductively coupled plasma – mass spectrometry), a method with improved performance compared to CE-ICP-MS, provides the means to separate and detect 20, 40, and 60 nm silver NPs simultaneously present in a mixture. However, the CE NPs separation mechanism is not completely understood until today [1]. The aim of this work was to try to answer some of the remaining questions: What is the role of sodium dodecyl sulfate (SDS) and the micelles during NPs separation? Do SDS molecules replace the surface coating during the separation or does the coating stay intact?

When an electric field is applied in CE, NPs move with different velocities through the buffer solution, and the mobility of the particles is proportional to their charge-to-size ratios. This unique separation principle allows to differentiate species with similar sizes but different charges. In the present work, silver NPs with comparable sizes and various surface coatings (citrate, polyvinylpyrrolidone (PVP), etc.) were successfully separated from each other after careful method optimization. Details of the experiments will be described. The ultimate goal is to obtain a deeper insight into the CE separation mechanism and to increase the usability of CE-SP-ICP-MS for more complex samples.

[1] B. Franze, C. Engelhard, *Anal. Chem.*, **86**, 5713-5720 (2014).

POSTER 2 - NANO: 9

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials, Environmental sciences
Keywords: CE-SP-ICP-MS, nanoparticles, separation, pre-concentration, surface coating

NEW POSSIBILITIES FOR ONLINE PRE-CONCENTRATION, SEPARATION, AND CHARACTERIZATION OF NANOPARTICLES IN COMPLEX SAMPLES WITH CE-SP-ICP-MS

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Engineered silver nanoparticles (NPs) find their use in consumer products and new technological developments more than ever before. Because particle properties and, most likely, the toxicity are size dependent, it is crucial to have sensitive and robust analytical techniques at hand, which are able to separate and detect NPs over a broad size and concentration range.

It was recently demonstrated that CE-ICP-MS (capillary electrophoresis – inductively coupled plasma – mass spectrometry) is an attractive tool for NPs separation [1]. However, certain aspects of CE including robustness and relatively small sample injection volumes in the nL-range have to be optimized before the method can be used routinely and at environmentally relevant concentrations.

In the present study, it is demonstrated for the first time how the limitation of small injection volumes can be overcome to a certain extent by using online pre-concentration in CE-ICP-MS. Specifically, a reversed electrodes polarity stacking mode (REPSM) approach was developed for silver nanoparticle analysis. Details of the approach and the influence of CE parameters on the performance will be discussed. Moreover, a home-built continuous data acquisition system with 5 µs time resolution [2] is applied to give single particle detection capabilities when performing CE. In CE-SP-ICP-MS (single particle ICP-MS), nanoparticles can be individually detected and separated from other sample constituents such as particles of different size or ionic counterparts in solution. Of course, one requirement for a successful analysis is that particle events do not overlap in a given detection window.

CE-SP-ICP-MS adds another dimension to CE analysis, as the NPs are separated not only in the migration-time dimension but also in the particle-size dimension. This helps to improve resolution and allows to study effects of CE conditions on the separation performance with high time resolution, i.e. individual ion clouds can be monitored. It is demonstrated that each NP size, the size distribution, and concentration can be obtained from an analysis of a NPs mixture. Using REPSM as a pre-concentration technique, the new CE-SP-ICP-MS method allows to detect Ag NPs in the sub-µg L^{-1} -range in a mixture of 20, 40, and 60 nm particles.

Additionally, a capability of CE for separation of silver NPs with different surface coatings (citrate, polyvinylpyrrolidone (PVP), etc.) is presented for the first time. This tool allows to extend the applicability of CE-SP-ICP-MS for speciation analysis of more complicated NPs mixtures.

[1] B. Franze, C. Engelhard, *Anal. Chem.*, **86**, 5713-5720 (2014).

[2] I. Strenge, C. Engelhard, *J. Anal. At. Spectrom.*, **31**, 135-144 (2016).

POSTER 2 - NANO: 10

Topics: Sample introduction and sample preparation, Nanomaterials
Keywords: single particle ICPMS, nanoparticles, microflow nebulizer

Sample introduction and calibration procedures for characterizing nanoparticulate suspensions by single particle ICP-MS

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Single Particle ICP-MS (spICP-MS) has received increasing attention for its potential to detect and characterize nanoparticle (NP) suspensions. This is achieved by observing 'pulses' in the ion beam signal intensity that occurs when a solid particle enters the plasma of the mass spectrometer and consequently delivers a cluster of ions to the detector of the instrument. The suitability of traditional methods for the sample introduction and calibration has not been extensively tested. Modified protocols are likely required to most reliably determine particle size, size distribution and particle number from pulses in the ion beam signal. Here we compare sample introduction and calibration approaches to determine suitable procedures and considerations for the analysis of NP suspensions.

All measurements were performed using an Agilent 7900 ICP-MS in time-resolved analysis mode with an integration time of 5 ms. Two configurations for sample introduction were assessed i) a conventional pneumatic nebulizer combined with a double pass spray chamber and ii) microflow nebulizer (DS-5, teledyne CETAC Technologies) in conjunction with a low volume (8 mL), total consumption single pass spray chamber. Well characterized and monodisperse NP suspensions with known particle number concentrations of Au (primary particle diameters 30, 60, 100 and 200nm) and Pt (primary particle diameters 30, 50 and 70 nm) were purchased from BBI Solutions and nanoComposix europe respectively. These stock suspensions are ideal test materials due to their well constrained and narrow size distribution, high purity, high density (19.32 and 21.45 kg/m^3 for Au and Pt respectively) and high abundance, interference free isotopes ^{197}Au (100%) and ^{195}Pt (33.8%). Traditional calibration methods using dissolved standards were applied to determine the mass of the analyte measured in the observed signal pulses and assess their suitability.

The transmission efficiency of particles was typically an order of magnitude higher, from approximately 5% to 50%, with the microflow nebulizer and single pass spray chamber relative to the more traditional sample introduction configuration. The measured signal from the dissolved calibration standards was suppressed relative to the signal measured from particles of equivalent analyte mass.

To avoid sampling bias in spICP-MS analysis high transmission efficiency sample introduction methods are likely to give the most reliable characterization of samples. Ionic solutions did not deliver the same signal intensity as a particle of equivalent mass, therefore calibrations established with well characterized particle suspensions are likely to be superior for spICP-MS analysis

POSTER 2 - NANO: 11

Topics: Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Nanomaterials
Keywords: nanomaterials, laser ablation, lung

Understanding silver nanoparticle deposition in rat following inhalation exposure using laser ablation-ICPMS

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Purpose: Human exposure to nanomaterials is increasing as a consequence of their growing number of products and applications. This increasing exposure is accompanied by concerns over safety in particular the potential toxicological consequences of their high bio-persistence in pulmonary tissues. We wished to investigate the pulmonary distribution of nanomaterials to determine where nanoparticle deposition is highest and therefore which cell model to utilise for in vitro studies.

Methods: Male Sprague-Dawley rats (250-320g) were exposed to spark generated silver nanoparticle (AgNP) aerosol via the nose-only route following neutralisation and diluted with oxygen and nitrogen to a final aerosol flow rate of 9 $Lmin^{-1}$. Animals were dosed for 3h/day for either 1 or4 consecutive days receiving concentrations of AgNP around 4.5 x 10^7 particles/cm^3 and mean particle sizes of 13.4 and 14.1 nm, respectively. Tissues were formalin fixed and stored as paraffin blocks until they could be analysed. Tissue slices (5µm) were mounted on slides, dewaxed and analysed for ^{107}Ag, ^{63}Cu, ^{66}Zn and ^{13}C using laser ablation-inductively coupled plasma mass spectrometry using a New Wave Research 213nm laser ablation system coupled to a Thermo iCAP Q ICPMS in KED mode. For comparisons between alveolar and bronchiolar levels of ^{107}Ag, line data was collected for 4 lines from a selected region containing both bronchiolar and alveolar tissue from 3 animals, data was then normalised against ^{13}C. Data was converted into a visual representation using Iolite v3.0.

Results: Distribution of nanoparticles in lung tissues is non-uniform. Imaging of whole lung samples demonstrates clear areas of greater nanoparticle deposition. When investigated further, the highest signal for nanoparticles is associated with lung macrophages. When bronchiolar and alveolar regions are compared, greater deposition appears to be within the bronchiolar region.

Conclusion: Laser ablation-ICPMS is able to clearly demonstrate the pattern of deposition of AgNP in tissue sections. The deposition of AgNP is non-uniform with greatest levels found in macrophages. With respect to pulmonary tissues, bronchiolar cells appear to be more highly exposed than alveolar cells. In vitro toxicological studies will focus upon use of bronchiolar and macrophage cell lines.

POSTER 2 - NANO: 12

Topics: Sample introduction and sample preparation, Elemental analysis, Nanomaterials
Keywords: Nanoparticles, ICP-MS, MVX-7100, Biological, Blood

The Quantification and Particle Sizing of Gold Nanoparticles in Biological Matrices Employing ICP-MS with Low Volume, Syringe Driven Sample Introduction Technology

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The need for the study of nanoparticle (particles with one or more external dimension falling within the range of 1 nm to 100 nm) exposure and the impact on human health has grown in recent years with the understanding of: i) natural nanoparticle occurrence in the environment; ii) the release of nanoparticles from industrial processes, combustion and human activity; iii) the manufacture and application of products and materials associated with nanoparticles. The most commonly used nanomaterials in consumer products are silver, titanium/titanium dioxide, carbon (nanotubes, nanofibres, fullerenes), silica, zinc/zinc oxide and gold. The use of these nanomaterials in consumer products has been of considerable concern to the toxicology community. This concern has led to proposals for restrictions due to their enhanced chemical properties and potential bio-persistence. Nanoparticles have the potential to cause both acute and chronic health effects as well as exacerbate underlying health conditions however they also have potential benefits. Future decisions upon their regulation would greatly benefit from understanding exposures to enable risk-based assessment of their toxicity.

To the analyst, nanoparticles pose a challenge as they can exist as unbound, agglomerate or aggregate forms. A number of strategies and analytical tools are available for the qualification and quantification of nanoparticles, however, all of these are made considerably more challenging when studying such particles in a biological matrix, i.e. in samples that can readily be taken from the body such as whole blood, blood plasma and urine. Accurate and precise data from such analyses is invaluable to the risk assessment of the potential detrimental health effects associated with particles of this nature.

In this presentation we describe the challenges associated with this type of analysis and the methodology of inductively coupled plasma mass spectrometry (ICP-MS) with low volume, syringe driven sample introduction technology for the concentration quantification and particle sizing of gold nanoparticles in whole blood, blood plasma and urine matrices. We describe the data generated from employment of this methodology and the benefits of such analyses in human health risk assessment strategies for nanoparticle exposure.

POSTER 2 - NANO: 13

Topics: Nanomaterials

Keywords: nanoparticle, microsecond, detection limit

Limits of detection for a wide range of metallic nanoparticles using Nu AttoM HR-ICP-MS with microsecond acquisition times.

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A wide range of nanomaterials have been developed for commercial applications because of the distinct electrical, optical and mechanical properties of the nanoparticles incorporated into their structure. However, the engineered nanoparticles (ENPs) associated with many of these products may be released in quantities that are harmful to human health or to the environment. To evaluate the potential risks of ENPs, the characterisation of these nanoparticles in environmental and biological matrices is of increasing importance. Inductively coupled plasma mass spectrometry (ICP-MS) is proving to be a useful tool for characterization and quantification of metallic nanoparticles. However, the short (150 – 400 ms) transient signals generated by single particle events present challenges to current ICP-MS instrumentation. The use of dwell times in the 50-100 µs range has overcome some of these challenges, but limitations in the sensitivity of quadrupole ICP-MS instruments makes the analysis of particles with diameters < 20nm particularly challenging. Characterisation of these smaller particles is critical for biological risk assessments.

This work presents particle size detection limits for several types of nanoparticles achievable with the AttoM HR-ICP-MS. The combination of high sensitivity and a fast data acquisition capability (10 us in continuous mode with no settling time) gives improved discrimination of particle events from the background, facilitating the measurement of the smallest nanoparticles. The automatic peak search with variable integration windows used to identify and integrate particle events also facilitates the characterisation of the smallest nanoparticles, compared to the conventional approach using fixed (dwell time) integration windows. Particle size detection limits for several metallic nanoparticles such as Au, Ag, CeO_2 (<5 nm) will be presented as well as more challenging ones such as TiO_2 and SiO_2. Improvements in the limits of detection for Fe_2O_3 nanoparticles have also been achieved using a pseudo resolution mode to resolve the $^{40}Ar^{16}O^+$ interference on ^{56}Fe.

POSTER 2 - NANO: 14

Topics: Elemental analysis, Laser-assisted analysis (LA, LIBS, LAMIS), imaging, biodistribution, Metallomics, Nanomaterials
Keywords: Silver Nanoparticles, LA-ICP-MS, Toxicology, Cosmetics, Tissue Samples

LA-ICP-MS in combination with traditional toxicology techniques to investigate in vitro percutaneous absorption of silver nanoparticles

C. Derrick Quarles Jr.[1], Maciej Stepnik[2], Katarzyna Domeradzka-Gajda[2], Beata Janasik[3], Wojciech Wasowicz[3], Jhanis J. Gonzalez[1,4]

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Consumer safety is of growing concern as it pertains to exposure to nanomaterials being used in everyday products, such as cosmetics. One of the most popular nanomaterial being used is silver nanoparticles, which has antibacterial properties but reports also suggest that after penetration of the skin it may induce some toxic effects. This report will investigate the ability of silver nanoparticles of different nominal size (15 or 45 nm) and structure (PEG or Citrate ligands) for potential penetration of isolated pig skin. Nanoparticles analysis was performed using UV-Vis spectroscopy, dynamic light scattering (DLS), and scanning transmission electron microscopy (STEM) techniques. Silver content was measured with ICP-MS while skin samples were investigated by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). In particular the added importance of LA-ICP-MS to the toxicology tool box will be highlighted.

POSTER 2 - NANO: 15

Topics: Nanomaterials

Keywords: nanoparticles, ICP-MS, ICP-QQQ, spICP-MS

Possibilities and Challenges of spICP-MS

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ICP-MS is a well-established and widely-used technique for measuring the dissolved elemental content of materials. More recently, there has also been growing interest in characterizing nanoparticles in various sample types.The relatively recent development of single particle ICP-MS (spICP-MS) is used to record the target element signals generated from individual NPs in the solution analyzed.

spICP-MS is the focus of attention because it allows simultaneous detection of the number, concentration, and size distribution of particles present, as well as the dissolved element concentration. In practice, however, there are some key factors that affect the true performance achievable for the measurement of NPs in real samples by spICP-MS:

1. The minimum detectable particle size is highly dependent on the sensitivity of the ICP-MS instrument used
2. The NP element(s) may also be present in the dissolved (ionic) state in the solution, and the concentration of the element in solution critically affects the particle size detection limit
3. The nebulization efficiency is a critical value required to calculate the size or concentration of NPs. The nebulization efficiency can most accurately be established by introducing NP reference materials with known concentration or size. However, the concentration of standard NPs reference materials is not always known and is subject to change with exposure to changing environmental conditions.
4. Quadrupole ICP-MS, like any scanning technique, is limited in its ability to accurately determine the concentration of multiple isotopes or elements in a single particle due to the very short duration of the nanoparticle plume.

When methods are developed and analytical expectations are defined for real sample measurements, it is important to correctly evaluate the accuracy and precision of spICP-MS and clarify the capabilities and challenges of the method.

In this work, we will present results from a study of the relationship between the sensitivity of ICP-MS and the size detection limit, as well as the influence of the ionic concentration on the size detection limit. The nebulization efficiency was evaluated for both ‘number based method’ and ‘size based method’ and the results from both methods were compared. Also, the possibility of the multiple element analysis by quadrupole ICP-MS will be discussed.

POSTER 2 - NANO: 16

Topics: Coupling techniques (chromatography, FFF, ETV, others), Nanomaterials, Metrology in chemistry
Keywords: single particle ICP-MS, field flow fractionation, nanoparticles, particle counting, particle sizing

Single Particle ICP-MS as an online detector for Field-Flow Fractionation

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One of the challenges in characterization of complex nanomaterials in the environment is to obtain number based information such as concentration and size distribution at environmentally relevant concentrations. The combination of Field-Flow Fractionation and Inductively Coupled Plasma Mass Spectroscopy (FFF-ICP-MS) has been proven to be an essential analytical technique for characterization of environmental samples, but it lacks a direct measurement of particle number.

Single Particle ICP-MS (sp-ICP-MS) is a new analytical technique to provide number based information for monodisperse metal and metal oxide nanoparticles at ppt concentration levels.

This presentation reports direct hyphenation of sp-ICP-MS to the Asymmetrical Flow FFF system. The sp-ICP-MS was utilized as an online number detector for characterization of a mixture of gold nanoparticles. The hyphenated technique was able to measure the number-based concentrations and size distributions of the nanoparticles by counting and sizing gold nanoparticles in the mixture, in a single run.

POSTER 2 - NANO: 17

Topics: Nanomaterials

Keywords: Aluminum SP-ICP-MS Artificial digestion Cellular uptake

Detection of aluminum nanoparticles in biological media and in vitro

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Aluminum is the third most abundant element in the earth crust and therefore ubiquitously detectable in the environment. Mostly found in the form of derivatives such as silicates or oxides, it also occurs as metallic aluminum for example as colorant in sweets or in aluminum foil.

With regard to potential toxicological effects, the different solubility of metallic aluminum nanoparticles compared to Al_2O_3 is of high relevance. Formation of ions may facilitate the crossing of blood-tissue barriers. Distribution towards other organs and subsequent re-formation of particulate aluminum due to milieu changes might occur. Therefore, the determination of solubility is required for proper risk assessment. Inductively coupled plasma mass spectrometry (ICP-MS) allows determination of aluminum with a detection limit of about 6 ppb. It could be proven that dissolution and solubility of metallic aluminum is significantly different when compared to Al_2O_3.

Using ICP-MS in the single particle mode, a significant change in the behavior of both aluminum species was detected after undergoing the artificial digestion. Nearly unchanged in the saliva, particles show dissolution and high agglomeration during the gastric state before deagglomerating again in the intestine.

Further analysis by time-of-flight secondary ion mass spectrometry (ToF-SIMS) revealed the uptake of both aluminum forms by proliferating and differentiated Caco-2 cells. For both particle forms different ions could be detected. Several aluminum-amino acid complex-derived ions from serine and valine were identified. In the case of Al_2O_3, $Al_2O_2^+$, $AlOH^+$, AlH_2O^+ and $Al[(H_2O)_6]^{3+}$ were the main ions found co-localizing within treated cells.

POSTER 2 - NANO: 18

Topics: Nanomaterials

Keywords: Hydrodynamic Chromatography, SP-ICP-MS, Au Nanoparticles, Lipid Vehicles

Development of a new Quantification concept for the Characterization of Nanoparticle Solutions with Hydrodynamic Chromatography connected to Single Particle Inductively Coupled Plasma Mass Spectrometry

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A growing number of engineered nanoparticles are being used in consumer products, such as, e.g.,cosmetics. As a result hereof, their potential to enter biological systems might possibly represent an risk of adverse effects to humans. The hazardous potential of nanoparticles (NP) depends on their properties, such as composition, size, shape and presence of ligands or coatings. Lipids for example are ingredients of numerous cosmetic products. Together with nanoparticles they form so-called vehicles, which contain an unspecific number of NP. At the same time, these structures with a size larger than 200 nm have a higher potential to enter cells and other biological systems compared to nanoparticles with classical coatings like citrate or polyvinylpyrrolidone. A selective and sensitive detection method for nanoparticles in such inorganic/organic particle clusters is essential for the analysis of the contained nanoparticles in terms of size, mass and agglomeration.

In this study, we have applied hydrodynamic chromatography (HDC), a technique suitable for sizing nanoparticles in a range between 5 to 300 nm, connected to an inductively coupled plasma mass spectrometer, used in single particle mode (sp-ICP-MS). By means of this HDC-mediated NP fraction separation, simultaneous analysis of material composition as well as size and number-based concentration was achieved.

Citrate stabilized gold (Au) nanoparticles of different sizes were used as a model system. In order to establish characterization metrics, three calibrations, each comprising two single experiments, were conducted in one measurement. The resulting ICP-MS raw data of each measurement were transformed into the three calibrations and into a contoured plot according the mass-size distribution of all particles analyzed.

Via prior and internal calibrations unknown monodisperse as well as polydisperse samples with the same NP material composition were analyzed successfully. Furthermore, the described method was used to analyze Au nanoparticles of different sizes in an organic encapsulation. Surprisingly between one and three particles were internalized per lipid vehicle.

POSTER 2 - VENDORS: POSTER SESSION 2: Vendors II

Time: Thursday, 23/Feb/2017: 3:40pm - 5:30pm

Location: ARLBERG-well.com FOYER

POSTER 2 - VENDORS: 1

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: soil, fertilizer, metals

Analysis of macro- and micronutrients in soils and fertilizers by ICP-OES

Nick Spivey[1], Ken Neubauer[1], Helmut Ernstberger[2]

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The drive for production of healthy and nutritious food requires knowledge about the quality of soils and fertilizers used for crop production. ICP-OES is typically the method of choice for this analysis due to its versatility and multielement capability, allowing the rapid screening of large sample numbers. Newly introduced ICP-OES instrumentation provides the flexibility to expand the upper range by element-specific signal attenuation whilst achieving high sensitivity with DualView technology. Here we report the results for a variety of soils from different provenance and a suite of consumer fertilizers. The samples were digested with a Titan MPS microwave digestion system and analysed on a PerkinElmer Avio200 ICP-OES. The sample preparation protocol and analysis method were validated with certified reference materials and spike recovery tests.

POSTER 2 - VENDORS: 2

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: food, electronic dilution, nutrients, trace elements

Analysis of trace elements and nutrients in food by ICP-MS

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The analysis of food for trace and nutritional elements is important to both inform and safeguard consumers. Label claims list nutritionally important elements, and regulations stipulate maximum levels for contaminant elements, which creates a need to establish and verify food quality. Traditionally, measurements of high levels and trace levels were approached with separate techniques: ICP-OES or flame AA for nutrients and ICP-MS for trace contaminants. Modern ICP-MS instrumentation provides a variety of features to enable the analysis of all constituents in a single run. Those features include interference reduction through collision and reaction modes, and the possibility to selectively attenuate high signals (i.e. electronic dilution) to bring signal intensities into the measurable range. Since electronic dilution is done on an element-by-element basis, it is possible to dilute high-level elements without the need for physical dilution. The detectability of trace elements is therefore not impaired. Here we report data for ICP-MS analysis of both trace and nutritional elements in food utilizing the full capabilities of ICP-MS.

POSTER 2 - VENDORS: 3

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: food, nutrients, ICP-OES

Food analysis for macro- and micronutrients with ICP-OES

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The analysis of food for micronutrient concentrations continues to be a prerequisite for establishing and verifying label claims, as well as documenting raw material quality for food producers. ICP-OES is frequently the method of choice for this analysis due its wide dynamic range and matrix tolerance. Here we report on the analysis by ICP-OES of a variety of food products, namely milk, milk powders and several juice products. The presented sample preparation protocols and analysis methods are verified by analysis of certified reference materials and spike recovery tests.

POSTER 2 - VENDORS: 4

Poster presentation (vendor paper)

Topics: Isotope ratio analysis, Plasma source fundamentals, instrumentation and mechanisms

Keywords: MC-ICP-MS, isotope ratio, abundance sensitivity, uranium, ion optics

Improvement in high mass abundance sensitivity for multicollector ICP-MS using a novel ion optics design that reduces several factors that contribute to peak tailing.

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Abundance sensitivity is a metric used to determine how much a mass of interest is influenced by a nearby mass of significant intensity. In magnetic sector ICP-MS where masses are separated by dispersion in a magnetic field, the tailing of an intense peak into the baseline of nearby masses can be influenced by several factors to do with the spread of ion energies, quality of the vacuum and beam disturbance due to space charge aberrations. A magnetic sector ICP-MS operates at a fixed resolution (typically 300-400 M/dM at 10% peak height) which means that at higher masses the signal peaks are physically closer together and therefore abundance sensitivity becomes a more critical parameter in the measurement of high dynamic range isotope ratios. A classical application where abundance sensitivity is crucial is for uranium isotope ratios, especially for ^{234}U and ^{236}U.

A novel ion optics design is available on the Nu Plasma 3 which provides a significant improvement in abundance sensitivity for uranium isotope measurement over and above the improvement seen when using the high abundance filter option previously available for Nu Plasma MC-ICP-MS. This work will describe some of the contributors to poor abundance sensitivity and the effect of the new design on these characteristics. Data will be presented on uranium standards to illustrate the improvement in accuracy seen with the new device available as the Enhanced Abundance Transfer Optic on the Nu Plasma 3.

POSTER 2 - VENDORS: 5

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation, Elemental analysis, Plasma source fundamentals, instrumentation and mechanisms

Keywords: Petrochemical, gasoline, ICP-OES, high resolution

Impurity Analysis in Low-Boiling Point Gasoline by High Resolution ARRAY ICP-OES

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Detection limits and method robustness achieved for the analysis of highly volatile organics by ICP-OES often hamper its applicability for impurity analysis on petrochemical plants. Hence, sample desolvation followed by ICP-MS analysis is often used, when conventional OES instruments lack sensitivity due to sample dilution and spectral interferences.

Here, we wish to report on the direct analysis of low-boiling point gasoline with both ppb_W detection limits e.g. for Arsenic and Vanadium, as well as excellent long-term performance without soot formation or memory effects. The impact of Oxygen addition on the precision of the Sodium and Potassium quantification will be discussed. The benefits of the high spectral resolution on the trace detection in presence of prominent carbon-based spectral signatures will be highlighted.

POSTER 2 - VENDORS: 6

Poster presentation (vendor paper)

Topics: Isotope ratio analysis

Keywords: isotope ratio, biological samples, interference management

Iron Isotope Rations in Biological Samples by PLASMAQUANT® MS

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To assess iron bioavailability, iron isotopes ratios were conducted in biological samples using the PlasmaQuant® MS. Optimization factors related to precision and accuracy of iron isotope ratios were optimized. Polyatomic ions (e.g., ArN^+, ArO^+, $ArOH^+$) and matrix polyatomic interferences (e.g., CaO and CaOH) were identified and significantly reduced using a “cool plasma” and hydrogen as a reactive gas in the integrated Collision Reaction Cell (iCRC). Isobaric interferences (e.g., $^{54}Cr^+$ on $^{54}Fe^+$ and $^{58}Ni^+$ on $^{58}Fe^+$) were minimized by equation correction and platinum sampler cones. Fe isotopic compositions of the samples were corrected for instrumental mass bias by the standard-sample bracketing method using the certified reference standard IRMM-014, after mineralization of the biological samples by microwave digestion. Precisions on the order of 0.05–0.20 (% RSD), 0.09–0.25 (% RSD), 0.30–0.40 (% RSD) and 0.12–0.26 (% RSD) were obtained for $^{54}Fe/^{56}Fe$, $^{57}Fe/^{56}Fe$, $^{58}Fe/^{56}Fe$ and $^{54}Fe/^{57}Fe$, respectively, in biological samples for ten replicates measurements. Such precision demonstrated that PlasmaQuant® MS, with its superior sensitivity, half argon-consumption, and its innovative interference management system, iCRC, it was able to eliminate or drastically reduce interferences, without the need of chemical samples purification. Such achievements allow iron isotope ratios determination in biological samples with precision between 0.05–0.40 (%RSD) for a low resolution collision/reaction ICP-MS system.

POSTER 2 - VENDORS: 7

Poster presentation (vendor paper)

Topics: Environmental sciences

Keywords: MP-AES, hydride generation, wine, arsenic

Routine Analysis of Total Arsenic in Californian Wines using the AGILENT 4200/4210 MP-AES

Courtney Tanabe[1,2], H Hopfer[1,2,3], Greg Gillegand[4], A Liba[4], S.E. Ebeler[1,2], Jenny Nelson[1,2,4], Elizabeth Kulikov[5]

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Wine is a globally consumed beverage where total levels of As are regulated between 100-200 µg L^{-1}, depending on the country in question [1]. However, there are countries, such as the United States, that do not regulate levels of all elements in wine. This necessitates investigating total As levels in wine produced in the United States to identify potential contamination, beyond the levels regulated by other countries. Measuring total arsenic levels in wine with various spectrometric techniques typically deliver insufficient sensitivity due to the element's relatively high ionization potential. However, the use of vapor generation techniques to form volatile forms of As allow for a more sensitive detection of As. This study investigates the use of the Agilent 4200

Microwave Plasma-Atomic Emission Spectrometer (MP-AES) coupled with the Multimode Sample Introduction System (MSIS) accessory, to assist with the production of hydride species, to measure total As in 40 wine samples from the California region.

A linear calibration for As, was obtained up to 100 µg L^{-1} with a calibration coefficient of greater than 0.999. The calculated Method Detection Limit (MDL) for As was 0.34 µg L^{-1}, at a confidence interval of 99.5%, resulting in a MDL approximately 100 times lower when compared to direct nebulization. Concentrations in samples ranging from below the MDL to 48.81 µgL^{-1}, well below the range of 100-200 µgL^{-1} regulated in many countries. The MSIS accessory provided easy and accurate analysis of total As in wine with spikes of 33 and 165 µgL^{-1}, in wines samples within 10% of expected values, with the exception of one which has a recovery on 111%.

REFERENCE: C. K. Tanabe, H. Hopfer, G. Gilleland, A. Liba, S. E. Ebeler and J. Nelson. Total arsenic analysis in Californian wines with hydride generation – microwave plasma – atomic emission spectroscopy (HG-MP-AES). J. Anal. At. Spectrom, 2016

POSTER 2 - VENDORS: 8

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation

Keywords: ICP-OES, productivity

Ultra-High Speed Analysis of Soil Extracts using an Advanced Valve System Installed on an AGILENT 5110 SVDV ICP-OES

Elizabeth Kulikov, John Cauduro

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Agricultural labs typically deal with high quantities of samples, however, higher analysis speeds normally create some sort of analytical compromise, such as reduced precision. The Agilent 5110 ICP-OES, combined with the fully integrated Advanced Valve System (AVS), does not compromise speed or precision. It is designed to deliver faster, cost effective and simpler sample analysis and is ideal for high throughput labs. This study describes the ultra-high speed

analysis of micronutrients Cu, Fe, Mn, Zn, Co, Ni and heavy metals Cd and Pb in a DTPA extracted soil sample using the Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES fitted with an integrated Advanced Valve System (AVS 6) six port switching valve.

The 5110 SVDV ICP-OES with AVS 6 analyzed 120 DTPA extracted samples and 6 standards in under 25 minutes. This equates to an average sample-to-sample analysis time of 11.7 seconds and an Ar consumption of only 3.4 L. Long term stability and precision of the AVS 6 was investigated to highlight that analytical performance is not compromised with higher analysis speeds. Long term stability was evaluated by analyzing a DTPA soil extract solution 120 times with all elements achieving less than 3.4 %RSD over the duration of the run, demonstrating the robustness required for soil samples of the 5110 ICP-OES over long sampling periods, not only delivering fast analysis times but without compromise to analytical results.

POSTER 2 - VENDORS: 9

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: ICP-OES, radial view, ASTM, oil, productivity

Improved Productivity for the Determination of Metals in Oil Samples using the AGILENT 5110 RADIAL VIEW (RV) ICP-OES WITH ADVANCED VALVE SYSTEM

Elizabeth Kulikov, Neli Drvodelic

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The ASTM Standard Test Method D5185-13 – Multi-element Determination of Used and Unused Lubricating Oils and Base Oils by ICP-OES – is a well established method for the rapid determination of 22 elements in used and unused lubricating oils and base oils, as well as rapid screening of used oils for wear-metals such as Fe, Cu and Al. Rapid completion of such analysis is essential for oil quality assurance and equipment condition monitoring. The Agilent 5110 Radial View (RV) ICP-OES, fitted with an Agilent SPS4 Sample Preparation System and the fully integrated Agilent Advanced Valve System (AVS 6) 6 port switching valve, was used to analyze the oil samples in accordance with the ASTM D5185 method. The 5110 RV ICP-OES, in conjunction with the AVS 6 was found to significantly improve productivity by reducing analysis time without compromising accuracy, precision, long-term stability and reproducibility.Linear calibrations for all elements were obtained up to 250 ppm, with correlation coefficients greater than 0.999. The vast linear dynamic range (LDR) of the 5110 RV permits reduction in the number of calibration standards, minimizing time spent on calibration and maximizing sample analysis time. Spike recoveries for all elements in used engine oil were within 10%, with an analysis time of only 22 seconds per sample. Decreased analysis times resulted in reduced argon gas consumption (only 7 L per sample) and thus significant savings for labs involved in high throughout analysis. Importantly, the increased productivity did not compromise reproducibility or long-term stability with less than 3% RSD and 10% concentration deviation over a 6 hour period, demonstrating the robust sample handling capability of the vertically-oriented plasma in the 5110 RV ICP-OES, even when analyzing challenging organic samples.

POSTER 2 - VENDORS: 10

Poster presentation (vendor paper)

Topics: Elemental analysis

Keywords: ICP-QQQ, reaction cell, high-purity metal, ultra-trace level impurities

Determination of ultra-trace level impurities in high-purity metal samples by ICP-QQQ

Naoki Sugiyama, Michiko Yamanaka

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Metals such as Cu, Al, Ta, W and Hf are used in interconnects, diffusion barriers and metalized thin films in semiconductor devices. Very high purity metals are required to ensure high performance, reliability and high production-yield of the devices. ICP-MS is a sensitive, multi-element technique used for the quality-control of these metal materials; but the application is not easy due to the requirement for ultra-low level impurity measurement in the relatively high-matrix metal sample digests.

A particular challenge is the ultra-trace measurement of alkali elements in the presence of the high matrix. Cool plasma is accepted in the semiconductor industry as a reliable technique to remove argon-based interferences such as Ar^+ and ArO^+ to enable low-level analysis of ^{40}Ca and ^{56}Fe. Cool plasma can also be applied to the analysis of the alkali and alkaline earth elements, providing lower background equivalent concentrations (BECs) than normal hot plasma conditions. This is because the low temperature plasma prevents the reionization of traces of the easily-ionized elements (EIEs) on the interface cones and ion lens. However, the cooler plasma also has poorer matrix tolerance, so is not suitable for the analysis of high matrix metals samples.

In this paper, we describe a new approach to the measurement of ultra-trace impurities in 0.1% high purity copper, using ICP-QQQ. The method uses a new design of ion lens that addresses the requirements of high matrix tolerance and ultra-low level measurement of the alkali and alkaline earth elements. The new lens, which is optional on the Agilent 8900 ICP-QQQ, has a unique geometry which minimizes background signals from EIEs on the skimmer cone. The new lens provides sufficiently high sensitivity to allow determination of ultra-trace impurities, combined with low EIE background signals under the hot plasma conditions required for high matrix analysis.

To provide a rapid method for production control and to minimize sample matrix loading, we investigated whether a single reaction cell mode could allow all elements to be measured free from interferences. A mixture of H_2 cell gas at 7 ml/min and O_2 at 0.23 ml/min was found to work well to remove all spectra interferences while maintaining good sensitivity for all measured elements. Using MS/MS mode on the 8900 ICP-QQQ eliminated the risk of interferences due to interelement overlaps or new, cell-formed product ions.

Details of the new method will be described, and figures of merit for the analysis of 50 elements in 0.1% high purity copper sample will be presented. The elements measured included the alkaline elements Li, Na and K, which can suffer elevated backgrounds due to reionization. Results will also be presented for elements that are difficult for conventional quadrupole ICP-MS (Si, S and P), and elements which suffer from Cu-based polyatomic interferences, such as Ru, Rh and Pd.

POSTER 2 - VENDORS: 11

Poster presentation (vendor paper)

Topics: Plasma source fundamentals, instrumentation and mechanisms

Keywords: Microwave Plasma, Emission Spectroscopy

Fundamental Studies of a Nitrogen Microwave Plasma for Analytical Emission Spectrometry

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The development of a microwave cavity with the ability to form magnetically excited high-power atmospheric pressure plasma using either air or N_2 support gas was reported in 2008 by Hammer.[1] The high stability and elliptical shape of this plasma, its robustness to a wide range of sample types and its significantly improved analytical performance led to its commercialization by Agilent Technologies in 2011 as a microwave plasma atomic emission spectroscopy (MP-AES) instrument.

We describe work carried out to characterise fundamental spectroscopic properties of this microwave plasma source for analytical emission spectrometry. We have combined chemical equilibrium modelling, using the NASA CEA free-energy-minimization program[2], with spectroscopic measurements of temperatures in a N_2 microwave plasma with aqueous sample introduction. We also describe experiments carried out using Thomson scattering to measure electron densities and temperatures in the plasma. The modelled electron densities, using as temperature inputs the electronic excitation temperatures derived from lines of Cr I, Fe I, and Ti I spectra (which are around 5000 K under typical operating conditions), are in good agreement with the data from the Thomson scattering experiments, which indicate an electron temperature of ~0.5 eV and an electron density of ~10^{19} m^{-3}. The plasma rotational temperature is also indicated, from measurements of the first negative system of N_2^+, to be around 5000-5500K, i.e., comparable to the electronic excitation temperature T_{exc}. Calculated ionic-to-atomic line ratios of selected elements, derived from the Saha-Boltzmann relation using modelled electron densities, are in good agreement with measured values.

Finally, complete spectra have been measured for a large number of elements, and comparison of these library spectra with spectra calculated using known spectroscopic constants (A-values, etc.) together with Saha-Boltzmann equation, and treating the ratio of excitation and electron temperatures as a freely adjustable parameter, indicates that the best fit between measured and synthetic spectra is obtained for a ratio of electron to excitation temperatures of approx. 1.06. Thus, present indications are that this plasma is fairly close to LTE.

References

1. M. R. Hammer, Spectrochim. Acta, 63B, 456 (2008)
2. https://www.grc.nasa.gov/WWW/CEAWeb/ceaHome.htm

POSTER 2 - VENDORS: 12

Poster presentation (vendor paper)

Topics: Isotope ratio analysis

Keywords: Gas Chromatography, Speciation, Sulfur, δ34S, MC-ICP-MS, Isotope Ratio, Crude Oil

Application of a new interface to the δ34S speciation analysis of volatile organic compounds in crude oil by GC-MC-ICP-MS.

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The measurement of the isotopic composition of individual compounds within a sample can potentially derive more information about the source of the sample and the processes it has undergone than simple bulk determination. The coupling of gas chromatography (GC) to multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) is potentially an efficient and effective analytical technique for isotope ratio speciation analysis. Here we report on the application of a new, commercially available, GC-MC-ICP-MS interface to $\delta^{34}S$ analysis of volatile organic compounds in crude oil.

The new GCI 300 interface consists of a simple, lightweight, flexible transfer line, facilitating easy coupling between the Thermo Scientific™ Trace 1300™ GC and Neptune Plus™ MC-ICP-MS. By maintaining a homogenous temperature profile, excellent GC peak definition is achieved, aiding compound identification and quantification, vital for a complex mixture such as crude oil. Amrani *et al* (2009)[1] pioneered GC-MC-ICP-MS for determining $\delta^{34}S$ of individual components in crude oil, which can contain weight percentage levels of sulfur. Subsequent GC-MC-ICP-MS has confirmed $\delta^{34}S$ fractionation between benziothiophenes (BTs) and dibenzothiophenes (DBTs) as indicative of petroleum samples which have undergone thermochemical sulfate reduction[2,3].

In our study, four crude oil samples were analysed by GC-MC-ICP-MS. Consistent retention times were used to identify 11 major component peaks which were present in all four samples: for which $\delta^{34}S$ values were calculated. The GC-MC-ICP-MS system was tuned by the addition of SF_6 and calibrated against four external sulfur-containing organic compounds.

In all four crude oil samples, an average 2-3‰ (5‰ maximum) $\delta^{34}S$ shift was observed between the BTs and DBTs organosulfur compounds. The degree of $\delta^{34}S$ shift observed for each compound was similar for each crude oil, suggesting a strong correlation between sulfur isotopic composition and the organic molecular structure of each compound. The overall range of $\delta^{34}S$ values in all four crude oils was over 16‰, reflecting the different geological source of each crude oil. Therefore, $\delta^{34}S$ speciation analysis could be used as a fingerprint to identify sources of crude oil.

1. A. Amrani, A. L. Sessions and J. F. Adkins, *Anal. Chem.*, 2009, **81**, 9027–9034.

2. S. Li, A. Amrani, X. Pang, H. Yang, W. Said-Ahmad, B. Zhang and Q. Pang, *Org. Geochem.*, 2015, **78**, 1–22.

3. Z. Gvirtzman, W. Said-Ahmad, G. S. Ellis, R. J. Hill, J. M. Moldowan, Z. Wei and A. Amrani, *Geochim. Cosmochim. Acta*, 2015, **167**, 144–161.

POSTER 2 - VENDORS: 13

Poster presentation (vendor paper)

Topics: Sample introduction and sample preparation

Keywords: acid digestion, ICP, pharmaceuticals

Alternative sample preparation and analysis approach for ICH/USP controlled metals by ICP-MS

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Digestion with strong acids is the common approach to prepare pharmaceuticals and their ingredients for the analysis by ICP-MS. For some materials this preparation might be difficult or impossible.

This Poster highlights the analysis of elemental impurities in pharmaceutical ingredients using the SQ- ICP-MS and adopting a unique organic solvent sample preparation method as per USP general chapters <232> and <233> as well as the related ICH methods.

The Poster will, along with the developed and optimized organic solvent method, discuss the analytical performance like precision, accuracy, repeatability.

Practical considerations for the analysis will also be presented.

POSTER 2 - VENDORS: 14

Topics: Elemental analysis

Keywords: infant formula, ICP-MS, quality control, trace and mayor elements analysis, single run

Simultaneous determination of various elements in infant formula using ICP-MS 2030

Ludivine Fromentoux[1], Jan Knoop[2], Uwe Oppermann[2], Konstantin Kartaschew[3]

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World demand for infant formula increases constantly, especially in Asia. To prevent baby intoxication, infant formula must be carefully analyzed. Determination of elemental composition is required in order to insure the high quality of this product. Due to various concentration levels of each element (trace or mayor), this analysis could be quite difficult to realize in only one measurement run.

A fast and easy method has been developed to quantify twenty different elements in infant formula using Shimadzu ICP-MS 2030. After simple sample acid digestion with nitric acid assisted by microwave, trace elements (Al, As, Cd, Cr, Cu, Fe, Hg, I, Mn, Mo, Pb, Sb, Se, Sn and Zn) and mayor component (Ca, K, Mg, Na and P) were quantified during one lone analysis sequence.

Thanks to an internal standard method and an efficient spectral interferences suppression (Kinetic Energy Discrimination KED), this method shows high accuracy and fidelity. Moreover, method development has been significantly simplified and accelerated using the exclusive software LabSolution ICPMS.

All measurements were conducted with a reduced gas consumption (-33%) because of the different ICPMS -2030 technical innovative solutions (minitorch, eco-mode…).

This different results testifies Shimadzu ICP-MS 2030 ability to be a valuable solution for infant formula analysis in quality control laboratories.

POSTER 2 - VENDORS: 15

Topics: Elemental analysis

Keywords: e-cigarettes, e-liquids, haeavy metals, ICP-OES

Determination of heavy metals in flavored e-liquids using ICP-OES

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Electronic cigarettes, nowadays called *e-cigarettes*, are an increasingly popular tobacco product that have still largely unknown public and individual *health* effects.

In European countries electronic cigarettes, such as e-pens, e-pipes, and e-cigars are widely used for inhalation of aerosols containing a mixture of nicotine and other substances instead of conventional cigarettes and cigars.

The major components of e-cigarettes is the flavored liquid contained in a cartridge. To create such a liquid, nicotine is extracted from tobacco and mixed with a base from propylene glycol and many other substances including a wide variety of flavors, colored substances and other chemicals.

Many e-liquids which are available in the European Union are manufactured on the highest quality standards and top level ingredients according to the manufacturers. The main ingredients, propylene glycol and vegetable glycerine are well known from a wide variety of everyday food products.

Article 20(10) of the European Directive 2014/40/EU1 ('Tobacco Products Directive' or 'TPD') requires the European Commission to submit a report to the European Parliament and the Council on the potential risks to public health associated with the use of refillable electronic cigarettes ('e-cigarettes'). The Commission has identified four main risks related to the use of refillable e-cigarettes.

These risks are: (1) poisoning from ingesting e-liquids containing nicotine (especially for young children), (2) skin reactions related to dermal contact with e-liquids containing nicotine and other skin irritants, (3) risks associated with home blending and (4) risks due to using untested combinations of e-liquid and device or hardware customisation. Member States and the Commission should carefully monitor the market of refillable e-cigarettes, as well as the notifications received under Article 20(2) of the TPD. Further research on certain aspects of e-cigarettes relevant to refillables, such as emissions testing and the safety of flavours or mixtures of flavours, should also be carried out. Additional research on these topics would benefit all users of e-cigarettes (disposable, rechargeable and refillable).

In this work a variety of e-liquids have been evaluated on their distribution of heavy metals. In order to monitor the element distribution the ICPE-9820 spectrometer with dual view optic has been used. Analytical results will be presented and advantages of the analytical method will be discussed.

References:

REPORT FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT AND THE COUNCIL on the potential risks to public health associated with the use of refillable electronic cigarettes (2016)

POSTER 2 - VENDORS: 16

Topics: Elemental analysis, Environmental sciences
Keywords: ICP-QQQ, Platinum Group Elements, Road Dust, MS/MS

Analysis of Platinum Group Elements (PGEs) in road dust using the Agilent 8900 Triple Quadrupole ICP-MS in MS/MS mode

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The monitoring of Platinum Group Elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt), Au and Ag has become of great interest in the environmental field as the presence of these elements in the environment has increased since the introduction of automobile catalytic converters. Thanks to its high sensitivity and multi-element capability, ICP-MS is widely used for quantification of the PGEs. However, the analysis of PGEs in soil and dust samples is challenging for conventional quadrupole ICP-MS due to the low concentrations of the elements, and the presence of several severe polyatomic interferences derived from the matrix. Examples include NiAr and NiCl on Ru-101, CuAr on Rh-103 and Pd-105, ZrO on Ag-107, and TaO on Au-197.

To remove the multiple, complex and variable interferences on the PGEs, and still be able to measure concentrations in the ng/L range in the digested samples, the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used in MS/MS mode, with ammonia as the reaction gas. To evaluate the quantification capabilities of the ICP-QQQ method, a certified reference material of road dust (BCR 723) was analyzed following acid digestion.

The high sensitivity, low background and unique interference removal capability offered by tandem mass spectrometry allowed the quantification of PGEs at ng/L level in a complex matrix.

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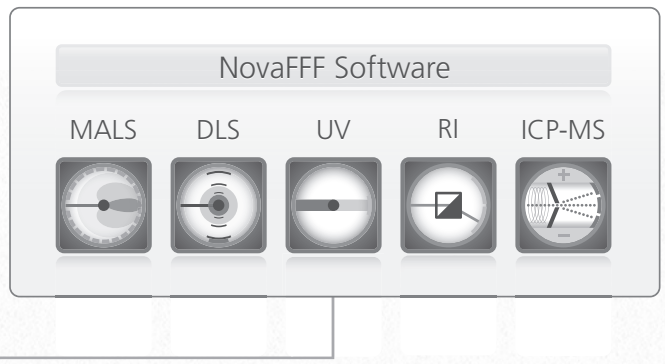

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“The world is more than the sum of single atoms.”

– Jimmy and Johnny

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